

## Irreversible phase transitions in a surface-reaction model with diffusion- and adsorption-limited reactions

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A model is proposed and studied for the heterogeneously catalyzed monomer-monomer reaction of the type  $A + B \rightarrow AB$ . In two dimensions, the active sites (AS's) of the catalyst belong to a (fractal) incipient percolation cluster, while the remaining surface, i.e., the inactive sites (IS's), is reaction passive.  $B$  adsorption is only allowed on AS's while IS's are embedded on a (fully)  $A$ -covered state.  $A$  monomers can diffuse from IS to AS and reaction takes place when  $A$  and  $B$  monomers are adsorbed on a pair of nearest-neighbor AS's. The model has a single parameter, namely, the adsorption probability of  $B$  monomers ( $p_B$ ). Starting from an empty configuration of AS's, two points  $p_{B1}$  and  $p_{B2}$  are found such that for  $p_B \lesssim p_{B1}$  ( $p_B \gtrsim p_{B2}$ ) the fractal cluster of AS's becomes poisoned by  $A$  ( $B$ ) monomers. For  $p_{B1} < p_B < p_{B2}$  the reaction reaches a stationary regime with  $AB$  production. So, both  $p_{B1} \cong 0.2075 \pm 0.0025$  and  $p_{B2} \cong 0.3600 \pm 0.0025$  are critical points at which second-order irreversible phase transitions take place. The dynamic critical behavior of the reaction is also studied and the obtained critical exponents strongly suggest that the model does not belong to the Reggeon-field-theory universality class, in contrast to rather well-established conjectures.

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### I. INTRODUCTION

Heterogeneously catalyzed processes involve various steps such as adsorption, surface diffusion, desorption, chemical reaction, etc., the latter being facilitated by the presence of the catalytic surface. These reaction processes have been studied extensively using numerous experimental techniques [1–3], while from the theoretical point of view most investigations are based upon classical mean-field models where averaged reactant coverages and reaction rates are considered [4]. Recent studies performed using lattice models, which account for microscopic details of the system under consideration, have revealed interesting features such as, for example, the role of fluctuations in the coverage of the reactants [5], the existence of anomalous or fractal reaction rates [6], segregation of the reactants [7,8], bistability and chaotic behavior [9,10], irreversible phase transitions (IPT's) [11–29], etc. Within this context, the study of IPT's has experienced considerable growth since the monomer-dimer lattice model introduced by Ziff, Gulari, and Barshad [11] to describe the oxidation of carbon monoxide. This monomer-dimer process has been studied by numerous authors, see, for example, [11–20], and references therein. Further studies on surface-reaction models exhibiting IPT's comprise the monomer-monomer [12,21–23], the dimer-dimer [24], the dimer-trimer [25] as well as various models where particles are spontaneously annihilated and autocatalytically created [26–28]. For a brief review see also [29].

The occurrence of IPT's is not restricted to surface-reaction processes. In fact, there are other nonequilibrium models, such as the contact process [30], Schlögl's first model [31], directed percolation (DP) [32,33], and

Reggeon field theory (RFT) [34] which also exhibit continuous IPT's from a configuration from which the system cannot escape, namely, the absorbing state, to an active state. The latter models belong to the same universality class and it has been conjectured [35,36] that all one-component models with a single absorbing state would belong to the universality class of the RFT or DP.

Grinstein, Lai, and Browne [15] have recently argued that the second-order IPT of the dimer-monomer surface-reaction process also belongs to the DP universality class. Their arguments can be generalized to systems with arbitrary numbers of chemical components, that is, continuous transitions into an absorbing state under generic conditions should belong to the DP universality class [15]. Critical exponents characteristic of the second-order IPT of the dimer-monomer reaction [16] are in excellent agreement with values obtained for directed percolation in  $2+1$  dimensions [33], confirming, at least for this reaction system, the conjecture of Grinstein, Lai, and Browne [15]. Furthermore, series expansion and simulation results reported by Dickman [26] indicate that various one-dimensional nonequilibrium lattice models in which particles are produced autocatalytically, and annihilated spontaneously, also belong to the DP universality class. Also, Jensen [28] has shown that a simple one-component surface-reaction model exhibiting a critical point, studied on fractal surfaces with fractal dimension  $D_F$  such that  $1 < D_F < 2$ , has critical exponents which interpolate between the values characteristic of DP in one and two dimensions.

The purpose of this work is to propose and study an alternative lattice model for the monomer-monomer reaction of the type  $A + B \rightarrow AB$ . While previous models are mainly based upon adsorption-reaction mechanisms

[11–25], the present approach incorporates different features. In fact, a connected set of active sites (AS's) with a random fractal structure is embedded in a (fully)  $A$ -covered sea of inactive sites (IS's). Adsorption of  $B$  monomers from the gas phase takes place only on AS's, while  $A$  species can diffuse from IS's to AS's and the reaction only occurs on the latter. This model is inspired by actual catalytic processes where the substrata are constituted by small fractal and catalytically active metallic particles finely dispersed on an inert matrix. The proposed model (for more details see Sec. II) exhibits two second-order IPT's from  $A$ - and  $B$ -poisoned states of the AS's to a stationary regime with  $AB$  production. The model is studied by means of the Monte Carlo simulation technique, which allows a detailed study of both the phase diagram and the relevant critical behavior of the system. The critical exponents of both IPT's of this model differ considerably from those characteristic of DP, suggesting that the transitions belong to another universality class.

## II. DESCRIPTION OF THE MODEL

### A. The substratum

Simulations are performed in two dimensions on the square lattice of side  $L$  ( $L \leq 200$ ), assuming periodic boundary conditions. The lattice has two kinds of sites, namely, AS's and IS's. AS's for the adsorption-reaction processes are those belonging to incipient percolation clusters (IPC's). IPC's obtained at the critical threshold  $p_c \cong 0.59275$  are fractal structures, with fractal dimension  $D_F = \frac{91}{48} \cong 1.9$ ; for reviews on the percolation theory see, for example, [37]. IPC's exhibit holes, branches, loops, and geometrical irregularities in all scales, so due to these interesting properties they have frequently been employed to simulate surface reactions in fractal media ([6,17–20] and references therein). Lastly, the remaining

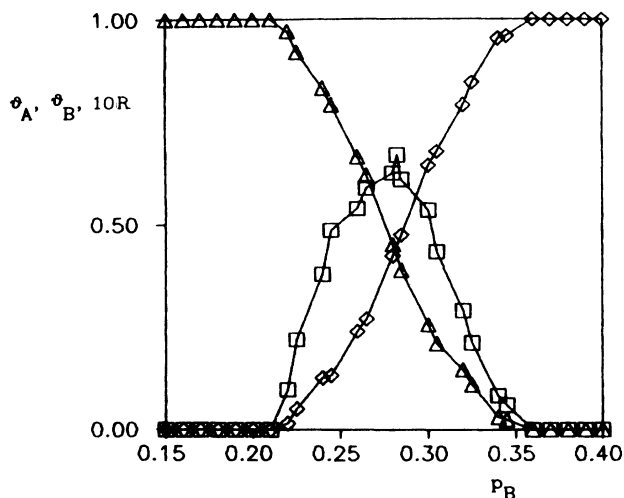


FIG. 1. Plots of  $\vartheta_A$  ( $\triangle$ ),  $\vartheta_B$  ( $\diamond$ ), and  $R$  ( $\square$ ) vs  $p_B$ . Lattice size  $L = 200$ , averages taken over  $10^2$  different configurations up to  $t = 10^4$ .

sites of the lattice, i.e., those which do not belong to the IPC, are the so-called IS's.

### B. The monomer-monomer reaction model

The lattice is assumed to be in contact with a reservoir containing  $B$  monomers.  $B$  species can only adsorb on AS's of the lattice with probability  $p_B$ , where  $p_B$  is the only parameter of the model. Adsorbed  $B$  monomers are not allowed to diffuse. On the other hand, IS's are embedded on a fully covered sea of  $A$  species. This species can diffuse onto the AS through the perimeter of the IPC. Once adsorbed on AS,  $A$  monomers are also allowed to diffuse at unit rate on them. Note that  $A$  monomers diffusing from IS's to AS's do not leave vacant sites behind because it is assumed that those sites are instan-

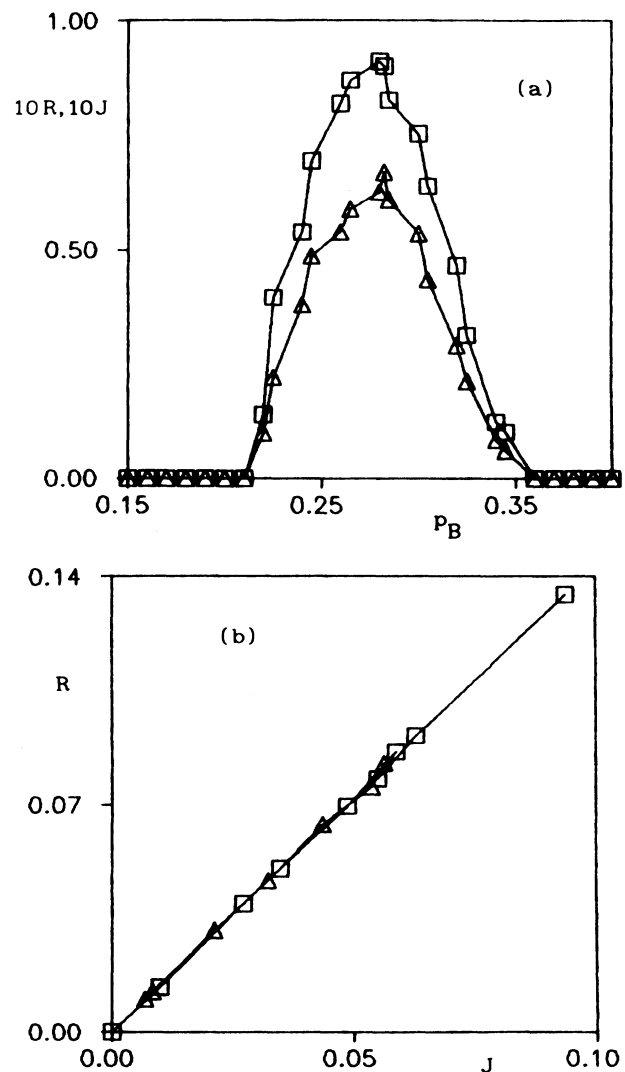


FIG. 2. (a) Plots of  $R$  ( $\triangle$ ) and  $J$  ( $\square$ ) vs  $p_B$  corresponding to the stationary regime. (b) Plot of  $R$  vs  $J$  for the stationary regime. ( $\triangle$ ) and ( $\square$ ) correspond to points at the left and at the right of the peaks shown in (a).

taneously covered by other monomers of the  $A$  sea. So,  $A$  monomers not placed on nearest-neighbor (NN) sites to the IPC perimeter are blocked, because they cannot diffuse.

Based upon the above assumptions, the Monte Carlo algorithm which describes the reaction process is the following. (a) A surface site is selected at random, then (b) if the site is occupied by a blocked  $A$  monomer of the  $A$  sea the trial ends and does not count for the evaluation of the Monte Carlo time. (c) If the site is occupied by an  $A$  monomer of the  $A$  sea capable of diffusing onto an AS or by an  $A$  monomer already adsorbed on an AS, a second NN site is selected at random. If that site is occupied by the trial ends (no diffusion). Otherwise, if the new site is empty (note that in this case the site must be an AS), the

monomer is allowed to diffuse with probability one. After this diffusion event all NN AS's are checked at random for the presence of  $B$  species.  $A$  and  $B$  monomers occupying NN AS's are removed, leaving two vacant AS's (infinite reaction rate). (d) If the selected site is a  $B$  monomer the trial ends because this species can neither desorb nor diffuse.

The Monte Carlo time step ( $t$ ) is defined such that, on the average, each site of the lattice is visited once. Runs are usually performed until  $t=10^4$ , unless poisoning occurs at early times.

During the simulation, relevant quantities such as the coverage with  $A$  ( $\vartheta_A$ ) and  $B$  species ( $\vartheta_B$ ), the rate of  $AB$  production ( $R$ ), and the flux of ( $J$ )  $A$  species per unit of time and perimeter length from IS to AS are recorded.

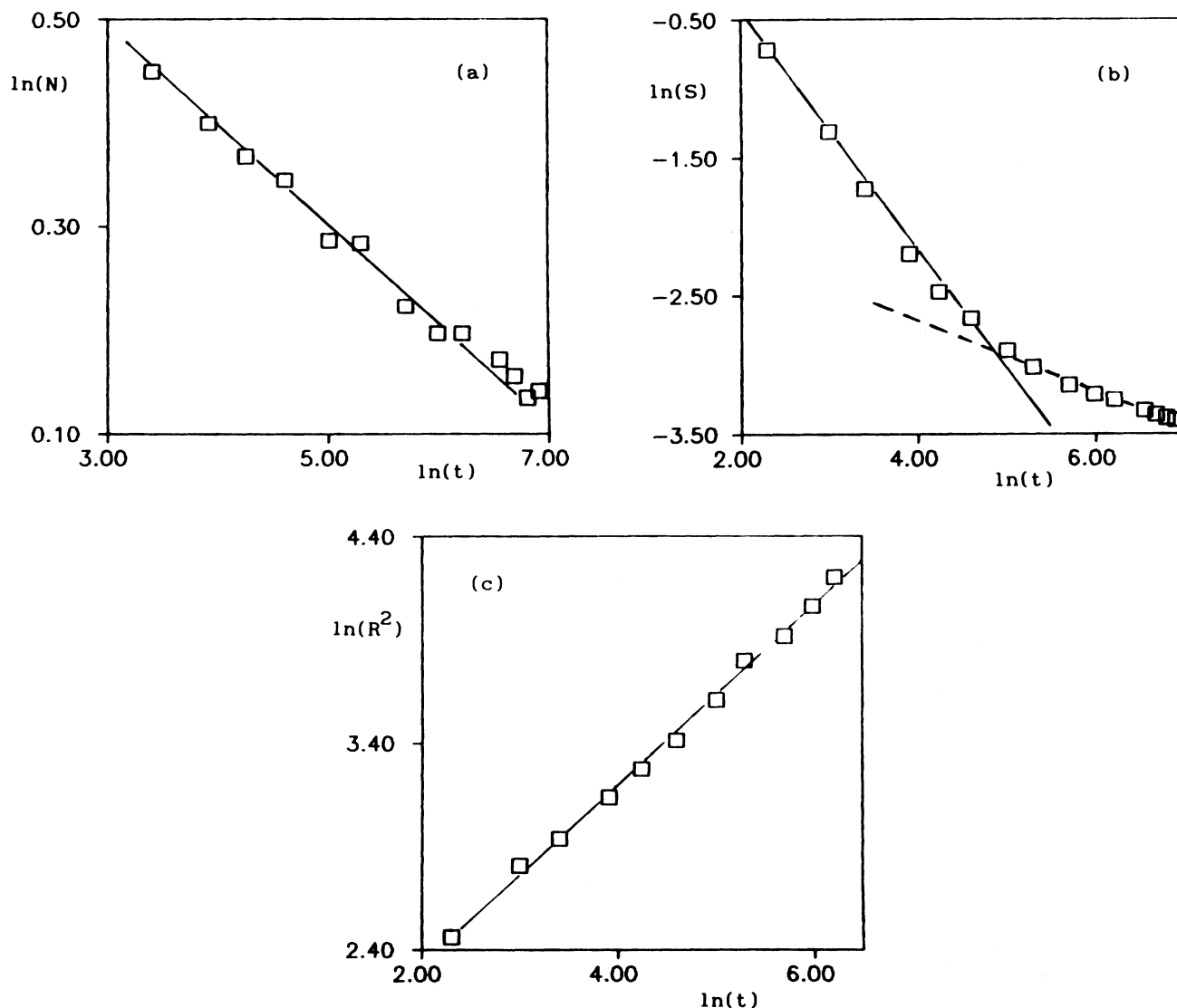


FIG. 3. In-ln plots of (a)  $N$ , (b)  $S$ , and (c)  $R^2$  vs  $t$  taken at  $p_{B1}=0.2075$ . Note in (b) that the slope crosses over from  $\delta \approx 0.88 \pm 0.02$  for  $t < 100$  (full line) to  $\delta \approx 0.29 \pm 0.02$  for  $t > 100$  (dashed line). Exponents obtained from the slopes of the straight lines are listed in Table I. More details in the text.

### III. RESULTS AND DISCUSSION

#### A. The phase diagram and the stationary regime

Figure 1 shows plots of  $\vartheta_A$ ,  $\vartheta_B$ , and  $R$  versus  $p_B$  corresponding to the stationary regime, i.e., the so-called phase diagram characteristic of the model. The existence of two critical points at  $p_{B1} \cong 0.2075 \pm 0.0025$  and  $p_{B2} \cong 0.3600 \pm 0.0025$  can clearly be observed (for a precise determination of the critical points see below). From Fig. 1 it follows that for  $p_B \leq p_{B1}$  ( $p_B \geq p_{B2}$ ) the sample becomes poisoned by  $A$  species ( $B$  species), respectively. On the other hand, for  $p_{B1} < p_B < p_{B2}$  a reactive reaction window with  $AB$  production is observed. The transitions from the poisoned states to the reactive regime are continuous, so one has two IPT's of second order. The existence of a finite-width reaction window between two

critical points is also characteristic of the dimer-monomer [11], the trimer-dimer [25], and some variants of the dimer-dimer [24] surface-reaction models.

Figure 2(a) shows plots of  $R$  and  $J$  versus  $p_B$  corresponding to the stationary regime. Both quantities have a peak close to the center of the window and are almost symmetric around it. The shape of the curves suggests a proportionality between  $R$  and  $J$  which is verified in Fig. 2(b). Therefore, once the system reaches the stationary regime, the rate of production is only limited by the flux of  $A$  species coming from the  $A$  sea and it is independent of  $p_B$ .

#### B. The dynamic critical behavior

As it has recently been demonstrated [16,23,25,28,29,33], a fruitful way to determine the

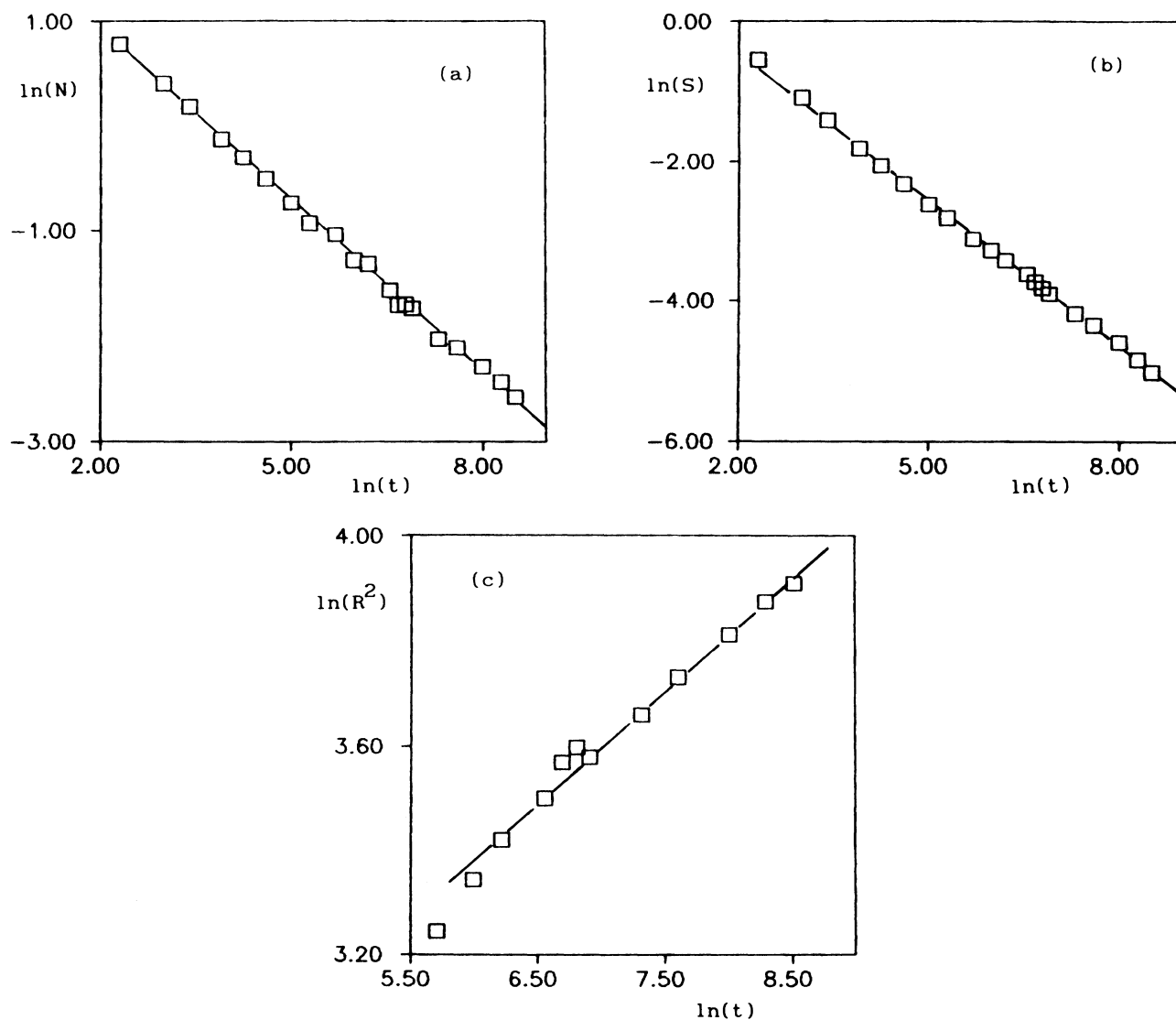


FIG. 4. In-ln plots of (a)  $N$ , (b)  $S$ , and (c)  $R^2$  vs  $t$  taken at  $p_{B1} = 0.3600$ . Exponents obtained from the slopes of the straight lines are listed in Table I. More details in the text.

TABLE I. List of critical exponents  $\delta$ ,  $\eta$ , and  $z$ , defined according to Eqs. (1)–(3). MM denotes the monomer-monomer model as studied in the present work (PW), DM denotes the dimer-monomer reaction process at  $p_1$  and  $p_2$ , second- and first-order IPT's, respectively, and DP denotes directed percolation in  $(n + 1)$  dimensions.

Model	$\delta$	$\eta$	$z$	Observations
MM on IPC	$0.29 \pm 0.02$	$-0.09 \pm 0.01$	$0.40 \pm 0.02$	PW, at $p_{B1}$
MM on IPC	$0.71 \pm 0.02$	$-0.54 \pm 0.01$	$0.28 \pm 0.02$	PW, at $p_{B2}$
DM on 2D	$0.452 \pm 0.008$	$0.224 \pm 0.010$	$1.139 \pm 0.005$	[16], at $p_1$
DM on 2D	3.70	-2.20		[38], at $p_2$
DP in (2+1)D	$0.460 \pm 0.006$	$0.214 \pm 0.008$	$1.134 \pm 0.004$	[33]
DP in (1+1)D	$0.162 \pm 0.004$	$0.308 \pm 0.009$	$1.263 \pm 0.008$	[28]

universality class of irreversible critical phenomena is to evaluate exponents related to the time-dependent critical behavior of the process. In the present simulations and close to  $p_{B1}$ , we begin with the AS's completely covered with  $A$  species except for a group of  $N_e$  empty sites, with  $2 \leq N_e \leq 9$  and  $\langle N_e \rangle \cong 5.07 \pm 1.69$ , which are selected close to the center of the IPC. Similarly, close to  $p_{B2}$  the AS's are covered with  $B$  species. The measured quantities are (i) the survival probability  $S(t)$ , that is, the probability that the sample was not poisoned after  $t$  time steps; (ii) the average number of empty sites  $N(t)$ ; and (iii) the average mean-square distance  $R^2(t)$  over which the empty sites have spread. Notice that  $N(t)$  is averaged over all samples, including those which have already been poisoned, while  $R^2(t)$  is only averaged over the runs in which the sample is not poisoned at time  $t$ . Averages are taken over  $5 \times 10^3$  samples, and runs are performed up to  $t = 10^3$  or  $5 \times 10^3$  in all cases. The lattice size is selected large enough, usually  $L = 100-200$ , in order to avoid the blob of empty sites to reach the boundaries. At the critical points it is expected that the following scaling laws should hold [16,23,25,28,29,33]:

$$S(t) \propto t^{-\delta}, \quad (1)$$

$$N(t) \propto t^\eta, \quad (2)$$

and

$$R^2(t) \propto t^z. \quad (3)$$

Results for the three quantities  $N(t)$ ,  $S(t)$ , and  $R^2(t)$  obtained for both critical points  $p_{B1} = 0.2075$  and  $p_{B2} = 0.3600$  are shown in Figs. 3 and 4, respectively. For  $p_B$  slightly smaller (greater) than the critical value the local slope of  $N(t)$ , for large  $t$ , veers downwards (upwards), respectively, allowing a very precise determination of the critical point [16,23,25,28,29,33]. In the present case the probability  $p_B$  is scanned in steps of  $\Delta p_B = 0.0025$ , so  $\pm \Delta p_B$  is the error in the determination of the critical points.

The best fits of the straight lines obtained in Figs. 3 and 4 allow us to evaluate the critical exponents listed in Table I, which also includes results obtained for other models for the sake of comparison. From these results it

follows immediately that the continuous IPT of the proposed monomer-monomer surface-reaction process does not belong to the DP universality class. In fact, as demonstrated by Jensen [28], critical exponents of the DP universality class determined using fractal substrata, with fractal dimensions  $1 < D_F < 2$ , nicely interpolate between values of these exponents for  $D_F = 1$  and 2. Obviously, this is not the case for the present model. Furthermore, the exponents  $\eta$  have a sign opposite to that characteristic of DP (see Table I). A change in the sign of  $\eta$  has also been found at the first-order IPT of the dimer-monomer surface-reaction process, suggesting the operation of a "spreading" mechanism [29,38].

Notice that the mean distance of spreading is measured simply using the Euclidean distance [28] and it is questionable whether this is a correct procedure for measuring distances between points on a fractal. Therefore it is expected that the errors in the exponents  $z$  should be greater than those listed in Table I. Nevertheless, in spite of this shortcoming one can assure that the model does not belong to the DP universality class because the other exponents, particularly  $\eta$ , are quite different (see Table I).

#### IV. CONCLUSIONS

A model for the monomer-monomer reaction of the type  $A + B \rightarrow AB$  is proposed and studied. The phase diagram shows that the model has two second-order IPT's between absorbing (poisoned) states and a reactive stationary regime. Evaluation of dynamic critical exponents of the model allows us to state that the proposed model does not belong to the universality class of DP. Since this universality class is quite robust, the understanding of the observed departure deserves further studies.

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