Critical Exponents for the Irreversible Surface Reaction $A + B \rightarrow AB$ with B Desorption on Homogeneous and Fractal Media

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A model for the surface reaction $A + B \rightarrow AB$ with B desorption exhibits a continuous irreversible phase transition from an A-poisoned state to a reactive regime. At criticality, an empty patch embedded in the poisoned state spreads on the sample following a random-walk diffusion behavior. So, a relationship between dynamic exponents of the reaction process, the random-walk exponent, and the fractal dimension of the substrate is conjectured and tested.

The kinetics of recombination processes has been intensively studied, both theoretically and experimentally ([1–12] and references therein). Within this context irreversible phase transitions (IPTs) in the monomer-monomer (MM) [2,6–8], dimer-monomer [2,5,9,10], and dimer-dimer [11] surface reaction processes have attracted considerable attention in recent years (for a brief review see Ref. [12]). Furthermore, there are other nonequilibrium models, such as the contact process [13], Schlögl's first model [14], directed percolation [15,16], and Reggeon field theory (RFT) [17], which also exhibit IPTs from a configuration from which the system cannot escape, namely, the adsorbing state, to an active state. The latter models belong to the same universality class and it has been conjectured [18,19] that all one-component models with a single absorbing state would belong to the universality class of the RFT. Grinstein, Lai, and Browne [9] have recently argued that the second-order IPT of the dimer-monomer surface reaction process also belongs to the RFT 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 RFT universality class [9]. Critical exponents characteristic of the second-order IPT of the dimer-monomer reaction [10] are in excellent agreement with values obtained for directed percolation in $2+1$ dimensions [16], confirming, at least for this reaction system, the conjecture of Grinstein, Lai, and Browne [9]. Furthermore, series expansion and simulation results reported by Dickman [20] indicate that various one-dimensional nonequilibrium lattice models in which particles are produced autocatalytically, and annihilated spontaneously, also belong to the RFT universality class.

In this work the time-dependent critical behavior of the MM surface reaction scheme, with desorption of one reactant, is studied. The MM surface reaction process is based upon the Langmuir-Hinshelwood mechanism [2,6–8]:

$$A(g) + * \rightarrow A(a), \tag{1a}$$

$$B(g) + * \rightarrow B(a), \tag{1b}$$

$$A(a) + B(a) \rightarrow AB(g) + 2*, \tag{1c}$$
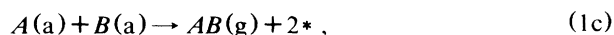
where (a) and (g) refer to the adsorbed and the gas phase, respectively, while $*$ denotes an empty surface site. Let p_B be the mole fraction of B species in the gas phase. Then, a monomer striking the surface could be a B with probability p_B or an A with probability $1 - p_B$. The model is simulated using the Monte Carlo technique employing three different substrata: one- (1D) and two- (2D) dimensional lattices, and incipient percolation clusters (IPCs) in two dimensions [21]. In all cases periodic boundary conditions are assumed. The simulation algorithm is the following: (i) A surface site is selected at random. (ii) Suppose that the site is empty. One attempts to adsorb A or B species using the striking probability already mentioned above. After an adsorption event all nearest-neighbor (nn) sites have to be checked in random order for the presence of adsorbed particles. If A and B are found occupying nn sites an AB species is desorbed leaving two sites of the surface free. Now suppose that the selected site is already occupied. If it is occupied by an A species the trial ends; otherwise, if it is occupied by a B species this particle is desorbed with probability 1, leaving an empty site on the surface. The Monte Carlo time unit (t) is defined such as each site of the surface is visited once, on the average. For more details see also [2,6–8].

Neglecting B desorption, the MM process exhibits an IPT at the critical point given by $p_{cB} = \frac{1}{2}$. That is for $p_B < p_{cB}$ $(p_B > p_{cB})$ the surface becomes poisoned by A (B) species [2,6–8].

Figure 1 shows the phase diagram of the MM process simulated on IPCs and obtained assuming B desorption. The latter assumption inhibits the formation of a B-poisoned state and consequently one observes a continuous second-order IPT from the A-poisoned state for $p_B \leq p_{cB}$ to a reactive state with AB production for $p_B > p_{cB}$. The IPTs occur at the critical points given by $p_{cB} \cong 0.5562 \pm 0.0003$, $p_{cB} \cong 0.5099 \pm 0.0003$, and $p_{cB} \cong 0.6150 \pm 0.0003$, for IPCs, 2D, and 1D substrata, respectively.

As has been demonstrated [5,10,16], a fruitful way to test the universality class is to evaluate exponents related to the time-dependent critical behavior of the process. In this case we begin with the 1D and 2D lattices completely
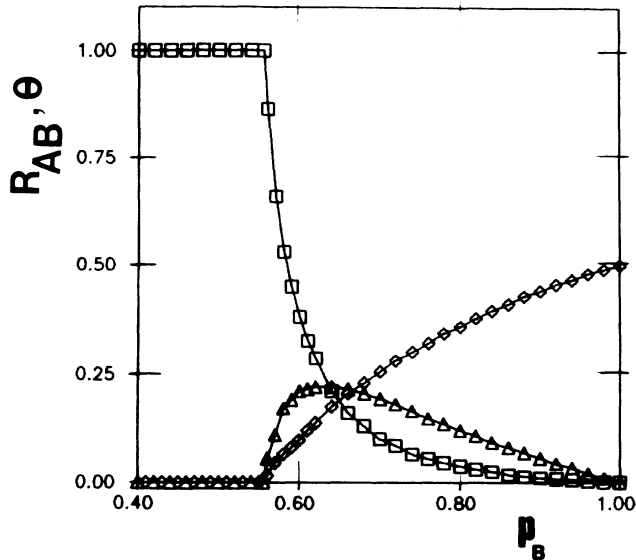

FIG. 1. Plot of the coverages with $A(a)$ and $B(a)$ species and the rate of AB production, θ_A ($\square$), θ_B ($\diamond$), and R_{AB} ($\triangle$), respectively, versus p_B for the MM surface reaction with B desorption on IPCs.

covered with $A(a)$ species except for a nearest-neighbor pair of empty sites at the center of the sample [5,10]. In the case of IPCs the simulations start similarly, but due to the disordered structure of the substratum a group of N_e empty sites, with $2 \leq N_e \leq 9$, are selected close to the center of the cluster. The resulting average number of empty sites is $\langle N_e \rangle \cong 5.07 \pm 1.69$. The measured quantities are as follows: (i) the survival probability $P(t)$, that is, the probability that the sample was not poisoned with $A(a)$ species after t time steps, (ii) the average number of empty sites $N(t)$, (iii) the average mean-square distance $R^2(t)$ over which the empty sites have spread, and (iv) the number of different sites $N_d(t)$ of the sample visited during the reaction process. $N(t)$ is averaged over all samples, including those which have already been poisoned, while both $R^2(t)$ and $N_d(t)$ are averaged over the runs in which the sample is not poisoned at time t [10,16]. Lattice sizes are selected large enough to avoid empty sites arriving at the boundary. Averages are taken over 4.5×10^3 (4.5×10^5) for IPCs (homogeneous) samples and runs are performed up to $t = 10^3$ in all cases. In spite of the fact that fluctuations for IPCs should be larger, results for these surfaces have poorer statistics because the generation of different IPCs for each case is quite time consuming. At the critical point it is expected that the following scaling laws should hold [10,12,16,17]:

$$P(t) \propto t^{-\delta},$$ (2)

$$N(t) \propto t^{\eta},$$ (3)

and

$$R^2(t) \propto t^z.$$ (4)

Furthermore, we conjecture

$$N_d(t) \propto t^x.$$ (5)

The fractal dimension d_f of the *part* of the sample visited during the reaction process at fixed time is defined as

$$N_d \propto R^{d_f},$$ (6)

and using Eqs. (4) and (5) one has

$$d_f = x/2z \leq D_f,$$ (7)

where D_f is the fractal dimension of the *whole* sample. Notice that both Eqs. (6) and (7) are valid in the limit of very low $B(a)$ coverage, because sites occupied by $B(a)$ species are considered in order to evaluate N_d but not to calculate R^2.

Results for the quantities $P(t)$, $N(t)$, $R^2(t)$, and $N_d(t)$ obtained for both 2D lattices and IPCs are shown in Figs. 2(a)–2(d), respectively. For p_B slightly smaller (greater) than p_{cB} the local slope of $N(t)$, for $t \to 10^3$, veers downwards (upwards), allowing a precise determination of the critical point [10,16]. The best fits of the data shown in Fig. 2 allow us to evaluate the critical exponents listed in Table I, which also includes results obtained for 1D samples. Results for the dimer-monomer surface reaction process and directed percolation are also listed in Table I for the sake of comparison. From these results it follows immediately that the continuous IPT of the MM surface reaction process with B desorption does not belong to the RFT universality class. The exponents obtained are also different from those reported for the first-order IPT of the dimer-monomer surface reaction process [5,12].

Using the exponents listed in Table I and Eq. (7) one obtains for the fractal substratum $d_f \cong 1.93 \pm 0.02$, in excellent agreement with the fractal dimension of IPCs given by $D_f = 91/48 \cong 1.90$ [21]. Also, for the homogeneous substrata one obtains $d_f \cong 2.08 \pm 0.02$ and $d_f \cong 1.06 \pm 0.02$, which again agree with $D_f = 2$ and $D_f = 1$, respectively. The slight overestimation of d_f could be due to the fact that Eq. (7) only holds in the limit of very low $B(a)$ coverage, as discussed above. These results indicate that the reaction spreads from the center over the neighboring regions of the sample, performing a compact visitation, that is, exploring all the accessible space. In order to gain insight into the visitation process, let us evaluate the average number of different sites visited per site unity $\langle n_d \rangle$, given with good approximation by

$$n_d \cong N_d/N \propto t^{x-\eta} \propto t^{d_s'},$$ (8)

where the time dependence is introduced via Eqs. (3) and (6) and $d_s' = x - \eta$. Using the values listed in Table I our estimate becomes

$$d_s' \cong 0.679 \text{ (IPCs)}, \quad d_s' = 0.98 \text{ (2D)}, \quad d_s' = 0.48 \text{ (1D)}.$$

These figures have to be compared with the random-walk exponent $\langle d_s \rangle$ [22]; i.e., the number of different sites
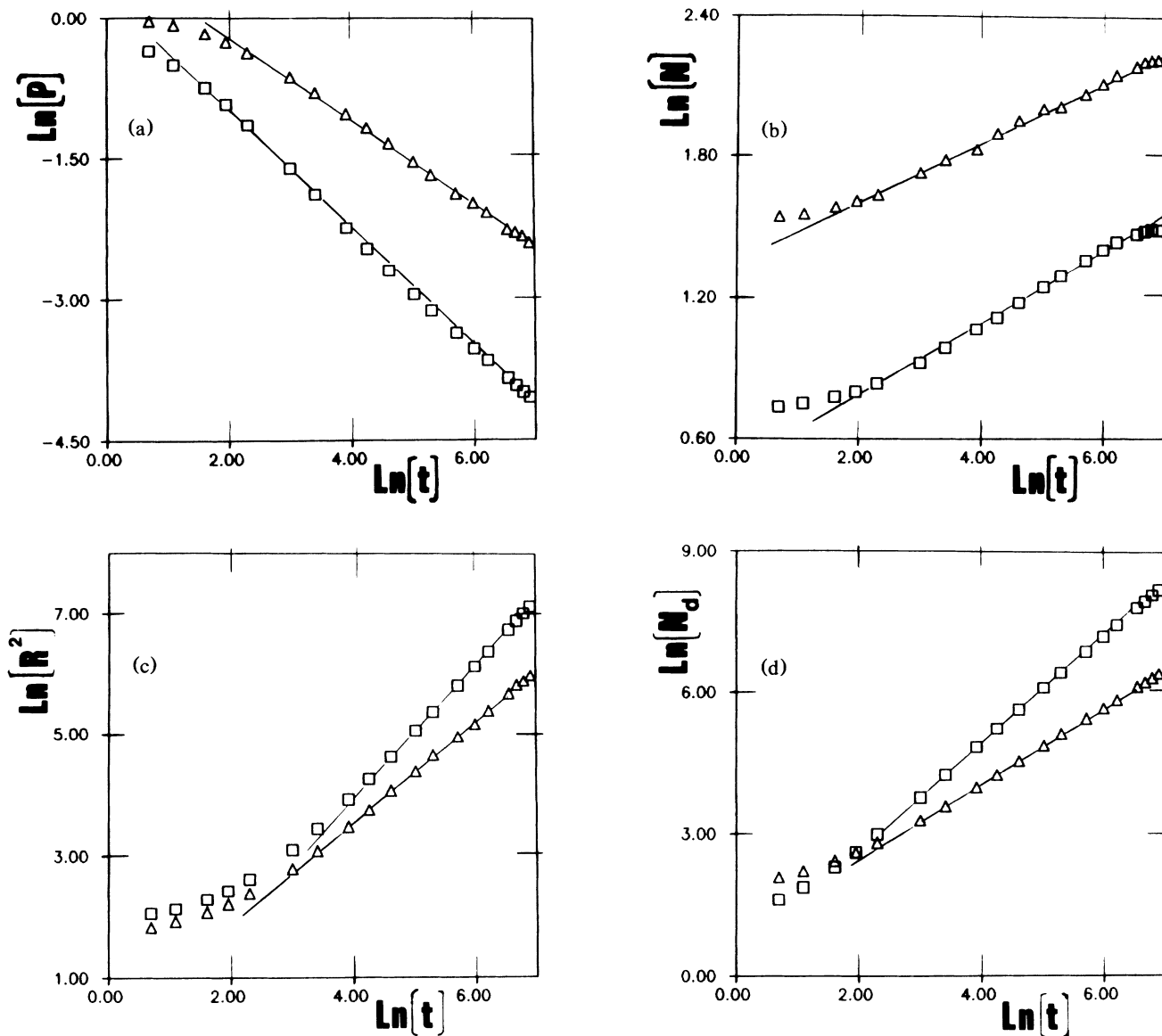
FIG. 2. Plots of (a) $\ln[P(t)]$, (b) $\ln[N(t)]$, (c) $\ln[R^2(t)]$, and (d) $\ln[N_d(t)]$ vs $\ln[t]$. Results correspond to simulations on IPCs ($\triangle$) at $p_{cB} = 0.5562$ and 2D media ($\square$) at $p_{cB} = 0.5099$. Straight lines are least-squares fits with correlation coefficients better than 0.999.

visited by a single random walk (S) at time t behaves as $S \propto t^{d_s}$:

$$d_s = \tfrac{2}{3} \text{ (IPCs, [22]),} \quad d_s = 1.0 \text{ (2D),} \quad d_s = \tfrac{1}{2} \text{ (1D)} .$$

Summing up, evidence is given to prove that the IPT of the MM reaction with B desorption does not belong to the RFT universality class, in contrast to the conjecture that continuous transitions into an adsorbing state of any system under generic conditions would belong to that universality class. Furthermore, in view of the obtained results, replacing d_f by D_f in Eq. (7) and d_s' by d_s in Eq. (8), the following conjecture, which relates the dynamic

exponents of the MM reaction process, the random-walk exponent, and the fractal dimension of the substrate, may be suggested:

$$zD_f = 2(d_s + \eta) . \tag{9}$$

This conjecture holds for the studied MM reaction process in both fractal and homogeneous media. The empty patch of the surface embedded in the poisoned state spreads via a random-walk diffusion process with compact visitation. From Eq. (9) also follows that the dynamic exponents η and z are not independent.

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TABLE I. List of critical exponents δ, η, z, and x, defined according to Eqs. (2)-(5). DM denotes dimer-monomer reaction process, DP denotes directed percolation in $2+1$ and $1+1$ dimensions, and PW denotes present work.

Model	δ	η	z	x	Ref.
MM on IPCs	0.449 ± 0.009	0.127 ± 0.011	0.843 ± 0.008	0.806 ± 0.007	PW
MM on 2D	0.632 ± 0.009	0.153 ± 0.010	1.091 ± 0.005	1.133 ± 0.006	PW
MM on 1D	0.223 ± 0.008	0.130 ± 0.010	1.211 ± 0.004	0.503 ± 0.005	PW
DM on 2D	0.452 ± 0.008	0.224 ± 0.010	1.139 ± 0.005	$\cdots$	[10]
DP in $(2+1)$D	0.460 ± 0.006	0.214 ± 0.008	1.134 ± 0.004	$\cdots$	[16]
DP in $(1+1)$D	0.162 ± 0.004	0.317 ± 0.002	1.272 ± 0.007	$\cdots$	[17]

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