Critical exponents for an irreversible surface reaction model

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A simple two-component irreversible surface reaction model introduced by Ziff, Gulari, and Barshad has been studied using computer simulations. The model has a second-order kinetic phase transition. We have determined some of the critical exponents and find that the model belongs to the universality class of Reggeon field theory and directed percolation.

Kinetic or nonequilibrium phase transitions have attracted considerable attention in recent years. A number of nonequilibrium models, such as the contact process,[1] Schlögl's first model,[2] directed percolation,[3] and Reggeon field theory,[4] exhibiting phase transitions and critical points, have been studied. A common feature of these models is that they contain a single component and exhibit a continuous transition from an absorbing state (a configuration from which the system cannot escape) to an active state. Results from computer simulations[5] and series analysis[4,6,7] have revealed that these and other models[6-10] belong to the same universality class. The models differ with regard to the local kinetic rules governing their time evolution. The critical behavior of Reggeon field theory is thus robust with respect to many different perturbations in the local kinetic rules. Grassberger[8] and Janssen[11] have conjectured that all one-component models with a single absorbing state belong to the universality class of Reggeon field theory.

In this paper we present results from a computer simulation of a two-component surface reaction model, proposed by Ziff, Gulari, and Barshad (ZGB),[12] which has been shown to exhibit a critical point. The study of this model is part of a larger program of identifying the possible universality classes of kinetic phase transitions.

The ZGB model is a simple model based on some of the experimentally[13] well-known steps in the oxidation of carbon monoxide on a catalytic surface:

$$CO(gas) \rightarrow CO(ads) , \tag{1}$$

$$O_2(gas) \rightarrow 2O(ads) , \tag{2}$$

$$O(ads) + CO(ads) \rightarrow CO_2(gas) . \tag{3}$$
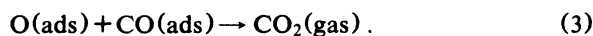
Here (ads) indicates that the particle is adsorbed on the surface. In the model the catalytic surface is represented by a square lattice. Each site can be either empty or occupied by an oxygen (O) atom or a carbon monoxide (CO) molecule. CO is added to the surface with the probability y_{CO} and is adsorbed if it strikes an empty site (process 1). O_2 is added with probability $y_O = 1 - y_{CO}$. If O_2 strikes a nearest-neighbor pair of empty sites, it dissociates into a pair of O atoms residing on separate (nearest neighbor) sites (process 2). After each adsorption process the neigh-

borhood of the newly adsorbed particle(s) is examined in order to determine whether any O-CO nearest-neighbor pairs were formed. If this is the case an O-CO nearest-neighbor pair is randomly selected, the O-CO pair immediately reacts and the CO_2 molecule thus formed desorbs at once, leaving two empty sites on which new molecules can be adsorbed (process 3). The only parameter in the model is y_{CO}.

The system defined by the rules mentioned above is manifestly irreversible. Results from computer simulations[12,14] have shown that the system always reaches a steady state, characterized by the average concentrations of adsorbed O atoms and CO molecules. The results are summarized in Fig. 1. The ZGB model has three phases: When y_{CO} is smaller than a critical value $y_1 \approx 0.390$, the lattice becomes completely covered with O atoms and all reactions cease (O-poisoned phase). Above a second value, $y_2 \approx 0.525$, the lattice becomes completely covered with CO molecules (CO-poisoned phase). Only in the case $y_1 < y_{CO} < y_2$ does the system reach a reactive steady state in which the reactions between CO and O can proceed indefinitely. The steady-state concentrations of O atoms, x_O, and CO molecules, x_{CO}, on the lattice change
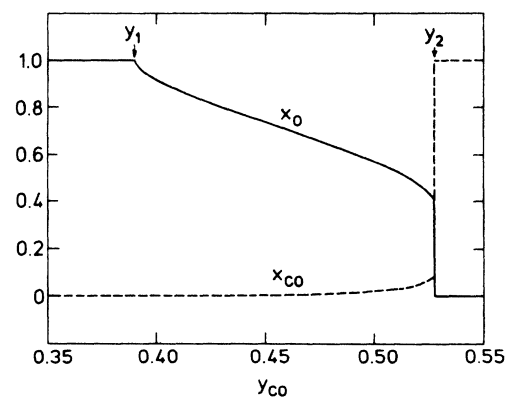

FIG. 1. Concentration of O (solid line) and CO (dashed line) on the surface as a function of y_{CO}. The system exhibits a continuous transition at y_1 from an O-poisoned state to an active state, and a discontinuous transition at y_2 into a CO-poisoned state.

continuously at y_1 and discontinuously at y_2. One may therefore characterize these as second- and first-order kinetic phase transitions, respectively. Note that, as in the models mentioned earlier, the transition at y_1 is a continuous transition from an absorbing state (the O-poisoned state) to an active state.

The qualitative features of the ZGB model are well reproduced by mean-field theory,[15] which also gives good quantitative results near the first-order transition. The second-order transition cannot be understood on the basis of mean-field theory. Meakin and Scalapino[14] found from computer simulations that near y_1 the steady-state concentrations of adsorbed O atoms and CO molecules scale like the following:

$$1 - x_O \sim (y_{CO} - y_1)^{\beta_O}, \text{ and } x_{CO} \sim (y_{CO} - y_1)^{\beta_{CO}}, \quad (4)$$

with $\beta_O \approx 0.61$ and $\beta_{CO} \approx 0.69$. The values predicted by mean-field theory[15] are $\beta_O = \beta_{CO} = 1$, indicating that the second-order transition is dominated by fluctuations and is not of mean-field character.

Grinstein, Lai, and Browne[16] have argued, on the basis of field-theoretical considerations, that the second-order transition of the ZGB model belongs to the universality class of Reggeon field theory and directed percolation. The known exponent[4] $\beta \approx 0.58$ for the Reggeon model in two dimensions is only marginally consistent with the numerical values obtained by Meakin and Scalapino. But it must be noticed that Meakin and Scalapino argue that their results indicate that $\beta_O = \beta_{CO}$. Therefore, it seems likely that the uncertainty in the numerical results is large enough to be consistent with $\beta = 0.58$. A simulation by Chopard and Droz[17] of a two-component stochastic cellular automaton exhibiting two continuous transitions into absorbing states yielded, for one of these, $\beta = 0.55 \pm 0.05$, which is again consistent with Reggeon field theory. Grinstein et al. generalize their arguments to systems with an arbitrary number of chemical components. They conjecture that the continuous transition of any such system from an absorbing state to an active state under generic conditions belongs to the universality class of Reggeon field theory. Even though the arguments of Grinstein et al. are quite convincing, direct numerical evidence is still needed in order to determine whether or not the ZGB model belongs to the universality class of Reggeon field theory.

In order to answer this question we made extensive simulations of the ZGB model near y_1. It is evidently quite difficult to obtain a precise value for the exponent β from steady-state simulations, as the large system sizes (needed to avoid fluctuations into the poisoned state) imply very long relaxation times near the critical point. One expects (steady-state) finite-size scaling analysis or time-dependent simulations to be more fruitful. Here we choose the latter method—recently applied by Grassberger to directed percolation in $2+1$ dimensions[18]—as it offers some insight into dynamical behavior. In the present simulations we begin with a lattice completely covered with O atoms except for a nearest-neighbor pair of empty sites at the center of the lattice. Starting from this configuration we made a number of independent runs, typically 100000 to 250000, for different values of y_{CO}
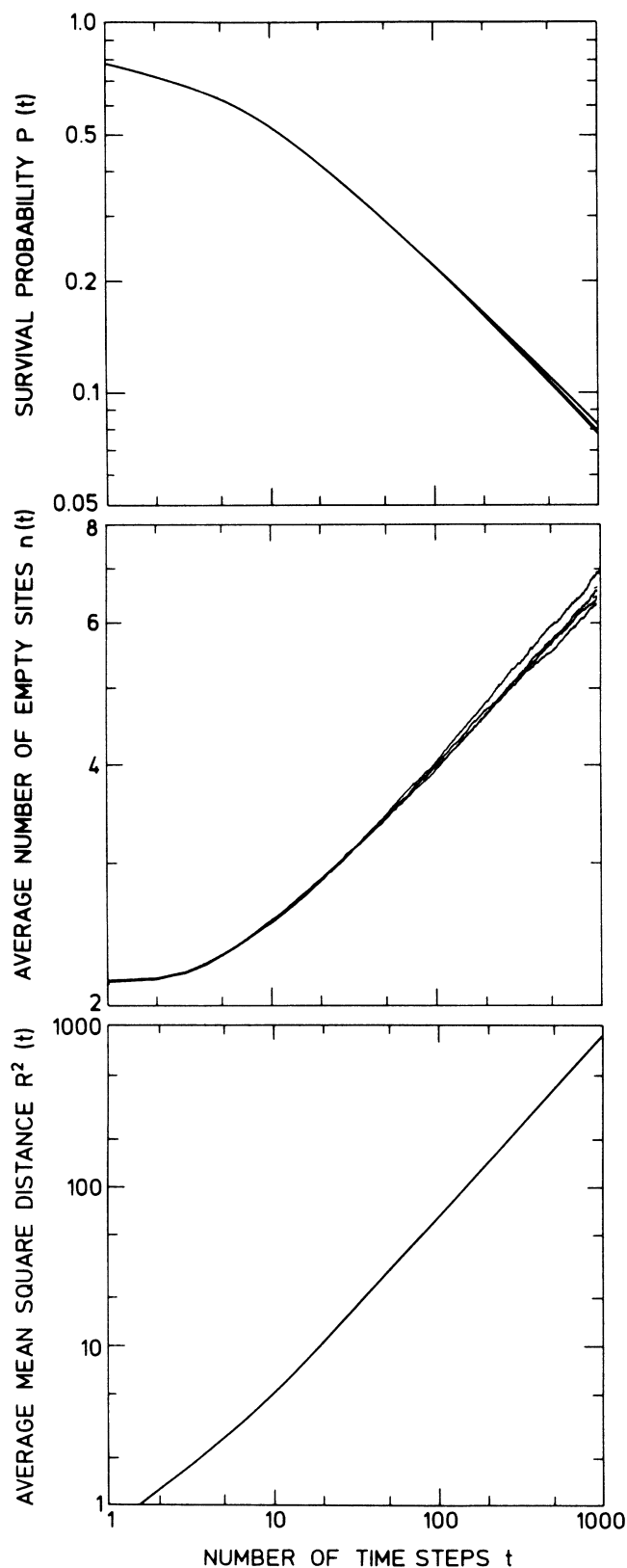

FIG. 2. Log-log plot of the survival probability (upper panel), the average number of empty sites (middle panel), and the average mean-square distance of spreading of empty sites (lower panel). Each figure contains four curves with, from bottom to top, $y_{CO} = 0.3905, 0.3906, 0.3907,$ and 0.3908.
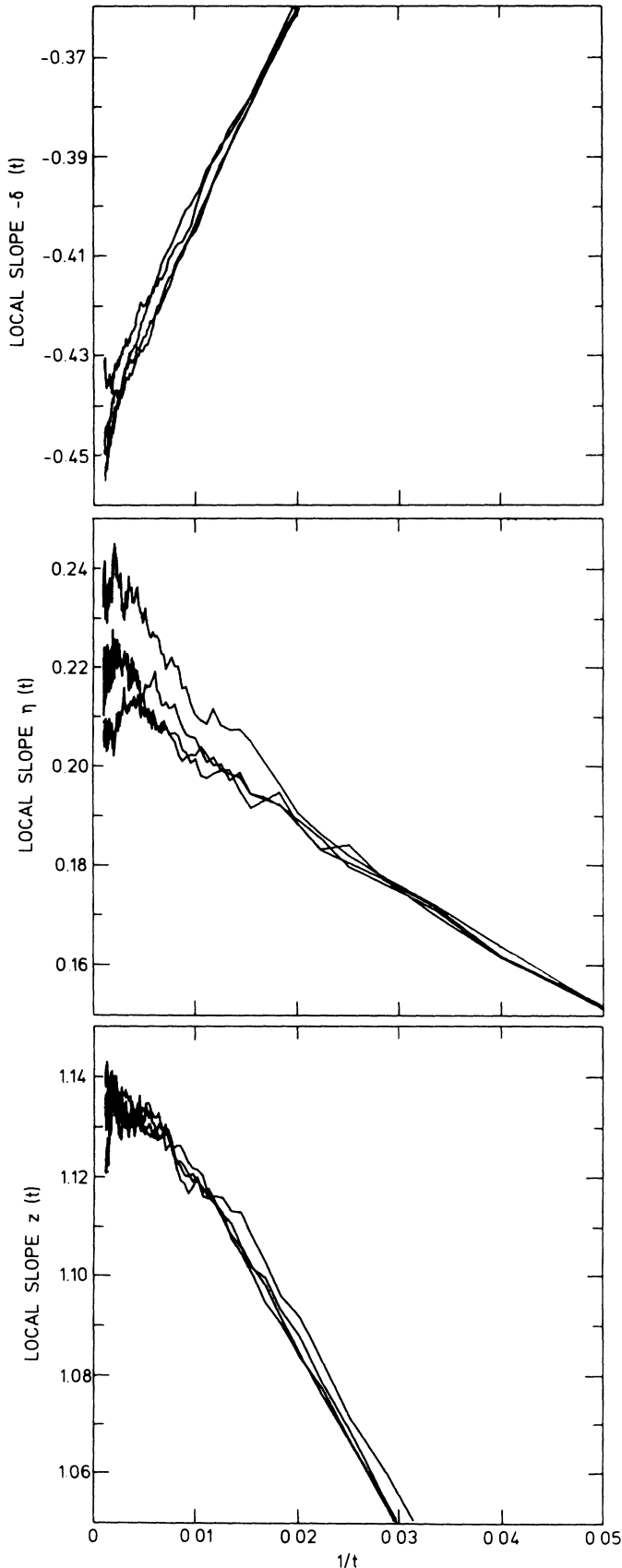
near the critical point. Throughout the simulations a list of empty sites was maintained and adsorption was only attempted on the sites known to be empty. For each attempted adsorption the time was increased by $1/M$, where M is the number of empty sites, which makes one time step equal to one attempted adsorption per lattice site. Each run had a maximal duration of 1000 time steps.

The quantities that we measured were (i) the survival probability $P(t)$, that is, the probability that the lattice was not poisoned with O atoms 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 had spread. It should be noticed that $n(t)$ is averaged over all runs, whereas $R^2(t)$ is averaged only over the runs in which the lattice was not poisoned at time t. At the critical point, $y_{CO} = y_1$, we expect (for large values of t) the scaling laws[18]

$$P(t) \sim t^{-\delta}, \tag{5}$$

$$n(t) \sim t^{\eta}, \tag{6}$$

and

$$R^2(t) \sim t^z. \tag{7}$$

Thus, when $y_{CO} = y_1$, graphs of $\ln(P)$, $\ln(n)$, and $\ln(R^2)$, vs $\ln(t)$ will asymptotically show a straight line (pure power-law behavior), while the off-critical plots will exhibit curvature. Our results for $P(t)$, $n(t)$, and $R^2(t)$ are shown in Fig. 2. More precise estimates for y_1 and the critical exponents can be obtained by looking at the local slopes of the curves shown in Fig. 2. The local slopes are defined as

$$-\delta(t) = \frac{\ln[P(t)/P(t/5)]}{\ln(5)}, \tag{8}$$

and similarly for $\eta(t)$ and $z(t)$. Grassberger has shown that the local slope $\delta(t)$ behaves as

$$\delta(t) = \delta + \frac{a}{t} + \frac{\delta'b}{t^{\delta'}} + \cdots, \tag{9}$$

and similar expressions for $\eta(t)$ and $z(t)$. Figure 3 shows plots of $-\delta(t)$, $\eta(t)$, and $z(t)$ against $1/t$. The middle panel of Fig. 3 clearly shows that the local slope $\eta(t)$ veers upwards for $y_{CO} = 0.3908$ and downwards for $y_{CO} = 0.3905$, indicating that $y_1 = 0.39065 \pm 0.00010$. Using Fig. 3 our estimate for the critical exponents becomes

$$\delta = 0.452 \pm 0.008, \quad \eta = 0.224 \pm 0.010, \quad z = 1.139 \pm 0.005. \tag{10}$$

These values for the critical exponents are in good agreement with the values obtained by Grassberger[18] for directed percolation in $2+1$ dimensions:

$$\delta = 0.460 \pm 0.006, \quad \eta = 0.214 \pm 0.008, \quad z = 1.134 \pm 0.004.$$

Our results show that the continuous phase transition found in the ZGB model belongs to the universality of directed percolation and Reggeon field theory. We believe that this provides substantial evidence in favor of the conjecture made by Grinstein et al. that the continuous transition into an absorbing state of any system under generic conditions belongs to the universality class of Reggeon field theory.

FIG. 3. Local slopes $-\delta(t)$ (upper panel), $\eta(t)$ (middle panel), and $z(t)$ (lower panel), as defined in Eq. (8), for the curves in Fig. 2.

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