

Critical Behavior of Surface-Reaction Models

Mann Ho KIM and Hyunggyu PARK

Department of Physics, Inha University Incheon, 402-751, Korea

We introduce a monomer-dimer catalysis model with variable excluded volume interactions between the same species. With infinitely strong interactions, this model exhibits a continuous transition from a reactive phase into an absorbing phase of monomers in one dimension. This absorbing state is identified as a doubly-degenerate state of monomers adsorbed in the alternating sites and vacancies in the other sites. We show numerically that the continuous transition from the reactive phase into this absorbing phase belongs to a new universality class other than the conventional one of the Reggeon field theory.

Many models have been proposed in recent years for the studies of various physical, chemical, and biological systems.^[1,2] Common features of these models are that they exhibit nonequilibrium phase transitions from a reactive phase into an inactive phase of a *single* absorbing state. Of these models, the contact process (CP)^[3] is supposed to be the simplest one which shows a nontrivial critical behavior. In the CP, a particle may be created with probability p at one of the neighboring sites of an existing particle or be annihilated with probability $1-p$. For sufficiently small p the system enters into an extinct state in the long-time limit, in which all lattice sites are empty so that the process ends forever. The extinct state is identified as a single absorbing state since there exists only one such state. The critical behavior of the CP has been shown to be equivalent to the directed percolation (DP) and the Reggeon field theory (RFT).

In order to describe the oxidation of CO on metal surfaces, Ziff, Gulari, and Barshad (ZGB)^[5] proposed a monomer-dimer model. In this model, a monomer (CO) adsorbs onto a single vacant site, while a dimer (O_2) adsorbs onto a pair of adjacent vacant sites and then immediately dissociates. A nearest neighbor of adsorbates, comprised of a dissociated O atom and an CO atom, reacts and forms a CO_2 molecule and desorb from the metal surface. In two dimensions, as the CO gas pressure is lowered, a first-order transition occurs from a CO-saturated inactive phase into a reactive steady state and then a continuous transition into a O_2 -saturated inactive phase. This continuous transition is also shown to belong to the RFT universality class.

Motivated by the monomer-dimer model, there have appeared many related lattice models to study nonequilibrium phase transitions. One of the simplest models is the monomer-monomer model^[6,7] in which particles of two different species can adsorb on a single vacant site with probability p and $q=1-p$. If two adsorbates of different species are nearest neighbors each other on

the surface, they react and form a product while desorb immediately from the surface. The system exhibits a first-order transition at $p=q=1/2$ from a phase saturated with one of two different species to another.

In both the monomer-monomer and the monomer-dimer models, interactions between adsorbing particles are ignored except for the actual surface reaction which converts the reactants into the product. Recently, there have been some efforts to investigate the effect of the nearest-neighbor interactions between particles of the same species on the critical behavior of the monomer-monomer model. In the "Dollars and dimes" model (Dd model),^[8] one of the species (dollar) has a diameter greater than a lattice spacing, so that the nearest-neighbor adsorbed dollars are not allowed and therefore the dollar-saturated phase does not exist. This Dd model is stoichiometrically the same as the monomer-monomer model but geometrically similar to the monomer-dimer model. Nevertheless, the critical behavior of the Dd model has been shown to be quite different from either the monomer-monomer or the monomer-dimer model. In one dimension, both the monomer-monomer and the monomer-dimer model exhibit a first-order phase transition, while the Dd model exhibits a continuous transition from a dime-saturated phase into a reactive steady-state phase which is found to belong to the RFT universality class.

A more generalized monomer-monomer model has been introduced^[9] where particles of the same species have *variable* repulsive interactions. This model interpolates between the simple monomer-monomer and the Dd model as the interaction strength is varied. When the interaction strength is weak, the interaction model exhibits only a first-order phase transition between two saturated phases of different species. At the critical value of the interaction strength, a first-order line terminates at a tricritical point beyond which two continuous-transition lines appear. The two saturated phases are

separated from a reactive steady state by these two lines. These two continuous transitions have been shown to be in the RFT universality class.

A common feature of the models mentioned above is that they exhibit, if any, a continuous-transition from a reactive phase into an inactive phase of a *single* absorbing state. The resulting critical behaviors are classified into the category of the so-called "DP conjecture"^[10-12] which depicts that models exhibiting a continuous-transition to single absorbing state generally belong to the universality class of the directed percolation (or the Reggeon field theory).

The universality of critical behavior for models with a single absorbing state is well established. But few studies have been made for models with more than one absorbing states. Very recently, as the counter examples of the DP conjecture, Jensen has extensively studied some nonequilibrium lattice models with infinitely many absorbing states.^[13,14] The pair contact process (PCP) is a simple one-component model in which a pair of adjacent particles may annihilate with probability p or create a particle at one of its nearest-neighbor sites with probability $1-p$. An absorbing state of the PCP is one without pairs. So there are infinitely many such absorbing states. Monte Carlo simulations have shown that there is a continuous transition from a reactive phase into an inactive phase of infinitely many absorbing states. Nevertheless, this continuous transition is shown to belong to the RFT universality class again. In addition, he also pointed out that the dimer-dimer model^[16] and dimer-trimer model^[17] which have infinitely many absorbing states might be in the RFT universality class, although heavy numerical errors obscured the fact, as if they were in the different universality class. His result seems to imply that the number of absorbing states of an inactive phase is not relevant to the universality class of nonequilibrium phase transition into an inactive phase. This shows a sharp contrast to the case of equilibrium phase transitions, where the number of ground states is relevant to the universality class. The symmetry between absorbing states may be more important than the number of absorbing states in determining the universality class of a nonequilibrium phase transition, which is also true in the equilibrium case. In the PCP, the infinitely many absorbing states are *not equivalent* probabilistically. Some absorbing states can be reached more easily than other absorbing states by the PCP dynamics. Therefore it is important to study a model with multiple *equivalent* absorbing states. As one of the simplest models with doubly degenerate absorbing states, we study the monomer-dimer model with infinitely strong repulsive interactions between the same species.

The interacting monomer-dimer model is a generalization of the simple monomer-dimer model, in which particles of the same species have nearest-neighbor repulsive interactions. This is parametrized by specifying that a monomer (A) can adsorb at a nearest-neighbor

site of an already-adsorbed monomer (restricted vacancy) at a rate $r_A k_A$ with $0 \leq r_A \leq 1$, where k_A is an adsorption rate of a monomer at a free vacant site with no adjacent monomer-occupied sites. Similarly, a dimer (B_2) can adsorb at a pair of restricted vacancies (B in nearest-neighbor sites) at a rate $r_B k_B$ with $0 \leq r_B \leq 1$, where k_B is an adsorption rate of a dimer at a pair of free vacancies. There are no nearest-neighbor restrictions in adsorbing particles of different species. The case $r_A = r_B = 1$ corresponds to the ordinary noninteracting monomer-dimer model which exhibits a first-order phase transition between two saturated phases in one dimension. In the other limiting case $r_A = r_B = 0$, there exists no fully saturated phase of monomers or dimers. However, this does not mean that this model has no absorbing states any more. In fact, there are two equivalent absorbing states in this model. These states comprise of only the monomers at the alternating sites of odd- or even-numbered lattice sites. There needs a pair of adjacent vacancies for a dimer to adsorb, so a state with alternating sites occupied by monomers can be identified with an absorbing state. It is noteworthy that these two absorbing states are configurationally the same as the doubly degenerate ground states of the Ising lattice gas.

In this paper, we consider the interacting monomer-dimer model with infinitely strong nearest-neighbor interactions only ($r_A = r_B = 0$). Then the system can be characterized by one parameter $p = k_A / (k_A + k_B)$ of the monomer adsorption-attempt probability. The dimer adsorption-attempt probability is given by $q = 1 - p = k_B / (k_A + k_B)$. The order parameter of the system is the concentration of dimers $\bar{\rho}$ in the steady state, which vanishes algebraically as p approaches the critical probability p_c from below:

$$\bar{\rho} \propto (p_c - p)^\beta, \quad (1)$$

where β is the order-parameter exponent. There is a spatial length scale, ξ , which diverges at criticality as

$$\xi(p) \propto |p_c - p|^{-\nu_\perp}, \quad (2)$$

where ν_\perp is a correlation length exponent in the space direction. It is quite difficult to measure the order parameter accurately near criticality by steady-state Monte Carlo simulations due to the critical slowing down. Moreover, there are strong finite-size effects near criticality because of the diverging correlation length. In this paper, we utilize the finite-size-scaling (FSS) idea developed for nonequilibrium phase transitions by Aukrust et al.^[18]

Various ensemble-averaged quantities depend on system size through the ratio of the system size and correlation length $L/\xi(p)$. Thus we can take the concentration of dimers near criticality as the following form:

$$\bar{\rho}(p, L) \propto L^{-\beta/\nu_\perp} f((p_c - p)L^{1/\nu_\perp}) \quad (3)$$

such that at p_c

$$\bar{\rho}(p_c, L) \propto L^{-\beta/\nu_\perp} \quad (4)$$

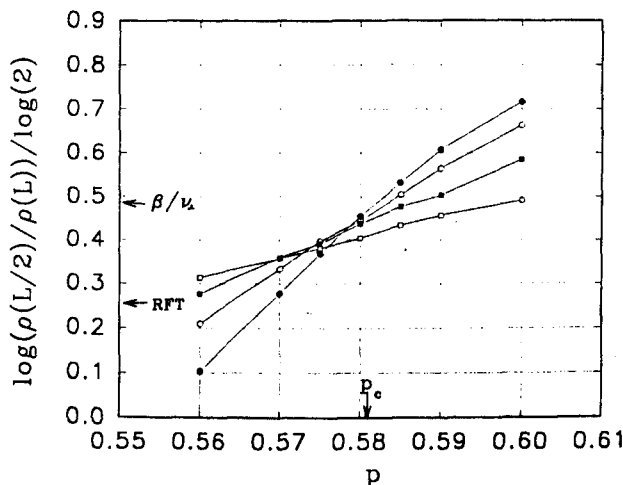


Fig. 1. Plots of $\log[\bar{\rho}(L)]/\log 2$ versus p . Open squares are for $L=64$, solid squares for $L=128$, open circles for $L=256$, and closed circles for $L=512$.

and

$$f(x) \propto x^\beta \text{ as } x \rightarrow \infty. \quad (5)$$

Eq. (3) reduces to Eq. (1) when the system size L goes to infinity near the critical point.

In the supercritical region ($p < p_c$), the concentration $\bar{\rho}$ remains finite in the limit $L \rightarrow \infty$, but it should vanish exponentially in the subcritical region ($p > p_c$):

$$\begin{aligned} \bar{\rho} &\sim \bar{\rho}_0 + b e^{-cL} & p < p_c, \\ &\sim b' e^{-c'L} & \text{for } p > p_c, \end{aligned} \quad (6)$$

where c, c' are constants and b, b' are algebraic functions of L . $\bar{\rho}_0$ is the steady-state concentration in the limit $L \rightarrow \infty$.

First, we run steady-state Monte Carlo simulations. The initial configuration is far from absorbing states with all sites vacated and we use periodic boundary conditions. Then the system evolves along the dynamical rules of our model. After one adsorption attempt on the average per lattice site (one Monte Carlo step), the time is incremented by one unit. The system reaches a quasi-steady state first and stays for a reasonably long time before finally entering into an absorbing state. We measure the concentration of dimers in the quasi-steady state and average over some independent samples which have not yet entered the absorbing states. The number of independent samples varies from 5×10^4 for system size $L=32$ to 10^4 for $L=512$. The number of time steps ranges from 500 to 10^4 and, at least, 500 samples survive until the end of simulations.

At p_c , we expect the ratio of the concentrations of dimers for two successive system sizes $\bar{\rho}(L/2)/\bar{\rho}(L) = 2^{\beta/\nu_1}$, ignoring the correction-to-scaling terms. This ratio converges to unity for $p < p_c$ and diverges to infinity for $p > p_c$ in the limit $L \rightarrow \infty$ (see Eq. (6)). We plot the logarithm of this ratio divided by $\log 2$ as a function of p for $L=64$,

128, 256, and 512 in Fig. 1. This plot shows strong corrections to scaling. The crossing points between lines of two successive sizes move to the right as the system size grows. In the limit $L \rightarrow \infty$, we estimate the crossing points converge to the point at $p_c \approx 0.581(2)$ and $\beta/\nu_1 \approx 0.48(2)$. The critical probability p_c can be more accurately estimated from the time-dependent Monte Carlo simulations which will be explained later. The value of the exponent ratio β/ν_1 is clearly different from the standard DP value of 0.2524(5) which is combined with $\nu_1 = 1.0972(6)$ and $\beta = 0.2769(2)$.

In order to measure the accurate values of p_c and dynamic critical exponents, we perform dynamic Monte Carlo simulations. We start with a lattice deposited by monomers at all odd-numbered sites except the center of the lattice which is vacant. The lattice is sufficiently large so that the initial defect cannot reach the boundary throughout the simulation. For each value of p investigated, 2×10 independent samples were simulated up to 8^3 time steps, though most runs stop earlier because the system gets into an absorbing state. The quantities that we measure are (i) the survival probability $P(2t)$, i.e., the probability that the system has not entered into the absorbing states at time t , (ii) the mean number of active vacancies, $N(t)$, which comprise of pairs of adjacent vacancies or single vacancies between A and B and (iii) the mean-square distance of spreading, $R^2(t)$, over which defects spread out. Following Grassberger and de la Torre,^[15] we get the following scaling laws at criticality

$$P(t) \sim t^{-\delta}, \quad (7)$$

$$N(t) \sim t^\eta, \quad (8)$$

and

$$R^2(t) \sim t^z. \quad (9)$$

At $p = p_c$, the values of $P(t)$, $N(t)$, and $R^2(t)$ scale algebraically in the long time limit and the double-logarithmic plots of these values against time fall on straight lines. Off criticality, they will exhibit some curvatures. More precise estimates for the critical exponents can be obtained by examining the local slopes of the curves. The effective exponents are defined as

$$-\delta(t) = \frac{\log[P(t)/P(t/b)]}{\log b} \quad (10)$$

and similarly for $\eta(t)$ and $z(t)$. In Fig. 2, we plot the effective exponents against $1/t$ with $b=10$. Off criticality these plots show upward or downward curvatures. From Fig. 2, we estimate $p_c \approx 0.581(1)$ which is consistent with our estimate from steady-state Monte Carlo simulations. The critical exponent is given by the intercept of the critical curve with the vertical axis. Our estimates for the critical exponents are

$$\delta = 0.29(2), \quad \eta = 0.01(2), \quad z = 1.39(3), \quad (11)$$

which deviate considerably from the RFT values:

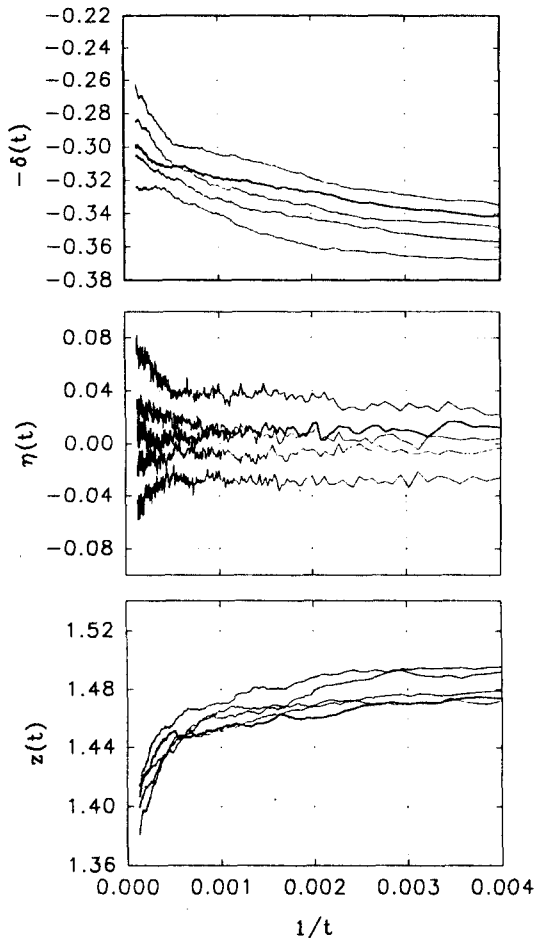


Fig. 2. Plots of the effective exponents against $1/t$. Five curves from the top to bottom correspond to $\phi=0.578, 0.580, 0.581, 0.582,$ and 0.584 . Thick lines are critical lines ($\phi=0.581$).

$$\delta=0.160(3), \quad \eta=0.317(2), \quad z=1.272(7). \quad (12)$$

In summary, we have numerically studied the interacting monomer-dimer model with infinitely strong repulsive nearest-neighbor interactions between the same species in one dimension. This model exhibits a continuous transition from a reactive phase to the absorbing phase with *two multiplicities*. The absorbing states comprise of monomers adsorbed on the alternating sites of a lattice, so that dimers do not have any room to be accommodated on the lattice. The obtained value of the exponent ratio, β/ν_{\perp} , is clearly different from the standard RFT value. Also the values of the dynamic exponents for this

model are far from the RFT values. Therefore we conclude that the continuous transition in our model belongs to a new universality class other than the conventional RFT class.

This result is contrast to the models with infinitely many absorbing states (e.g. PCP) which have been shown to be in RFT universality class. We emphasize that the symmetry between absorbing states is more important than just the number of absorbing states in determining the universality class of a nonequilibrium phase transition into an inactive phase.

This work is supported in part by the Korean Science and Engineering Foundaiong Foundation (No. 931-02 00-019-2) and in part by the BSRI, Ministry of Education, Korea.

REFERENCES

- [1] T. H. Liggett, *Interacting Particle Systems*, (Springer-Verlage, New York, 1985).
- [2] H. Haken, *Synergetics*, (Springer-Verlag, New York, 1983).
- [3] T. E. Harris, *Ann. Prob.* **2**, 969 (1974).
- [4] P. Fisher and U. M. Titulaer, *Surf. Sci.* **221**, 409 (1989).
- [5] R. M. Ziff, E. Gulari and Y. Barshad, *Phys. Rev. Lett.* **56**, 2553 (1986).
- [6] P. Meakin and D. J. Scalapino, *J. Chem. Phys.* **87**, 731 (1987).
- [7] R. M. Ziff and K. Fichthorn, *Phys. Rev.* **B34**, 2038 (1986).
- [8] H. Park, J. Köhler, I.-M. Kim, D. ben-Avraham and S. Redner, *J. Phys.* **A26**, 2071 (1993).
- [9] J. Zhuo and S. Redner and H. Park (to appear in *J. Phys. A*).
- [10] H. K. Janssen, *Z. Phys.* **B42**, 151 (1981).
- [11] P. Grassberger, *Z. Phys.* **B47**, 365 (1982).
- [12] G. Grinstein, Z.-W. Lai and D. A. Brown, *Phys. Rev.* **A40**, 4820 (1989).
- [13] I. Jensen, *Phys. Rev. Lett.* **70**, 1465 (1993).
- [14] I. Jensen and R. Dickman (to be published).
- [15] P. Grassberger and A. de la Torre, *Ann. Phys. (NY)* **122**, 373 (1979).
- [16] E. V. Albano, *J. Phys.* **A25**, 2557 (1992); A. Maltz and E. V. Albano. *Surf. sci.* **277**, 414 (1992).
- [17] J. Köhler and D. ben-Avraham, *J. Phys.* **A24**, L621 (1991); D. benAvraham and J. Köhler, *J. Stat. Phys.* **65**, 839 (1992).
- [18] T. Aukrust, D. A. Browne and I. Webman, *Phys. Rev.* **A41**, 5294 (1990).