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Absorbing-State Critical Phenomena in Interacting Surface Reaction Models

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Absorbing-state critical phenomena in various surface reaction models are briefly reviewed, focusing on their universal properties. The directed percolation universality class and the directed Ising universality class are identified, associated with absorbing-state phase transitions in these one-dimensional reaction models.

I Introduction

During the last decades, nonequilibrium critical phenomena have been extensively studied in various areas such as epidemiology, biology, chemistry, sociology and physics [1-4]. An interesting example of nonequilibrium phase transitions is the absorbing phase transition. In this case, there exist some absorbing (trapped) states in configurational phase space. If the system gets into one of these absorbing states by the evolution dynamics, then the system is trapped: no further dynamics can occur, to escape from the absorbing state. By controlling an external parameter, the system may undergo a continuous phase transition from an active steady-state phase into an inactive absorbing phase. In the active phase, the system manages to avoid the traps so it has a finite probability to stay alive forever.

Recently, various kinds of nonequilibrium lattice models exhibiting absorbing transitions have been studied extensively [3-6]. These models describe a wide range of phenomena, in particular, epidemic spreading, catalytic chemical reactions, and transport in disordered media. Two distinct types of absorbing phase transitions have been identified in one dimension: the directed percolation (DP) and directed Ising (DI) universality class. Most models have been found to belong to the DP class [7-13], which involves typically a single absorbing state or multiple absorbing states with one of them dynamically more prominent than the others (no explicit symmetry). DI type critical behavior appears in models with two equivalent absorbing states or two equivalent classes of absorbing states (Ising type symmetry) [14-21]. The degeneracy of the absorbing states may be obscured by an alternative representation of the models. By assigning kinks (or particles) between different absorbing domains, the multiple absorbing states correspond to a single vacuum configuration and their degeneracy translates into particle-number conservation. For example, in the dynamics of branching annihilating random walks (BAW) [22-25], the vacuum (absorbing) state is not degenerate, but the absorbing transition belongs to the DI class if the dynamics conserve the particle number modulo 2. So the DI class is sometimes called the PC (parity-conserving) universality class.

In this paper, we focus on nonequibirium surface reaction models exhibiting absorbing transitions. In Sec. II, we discuss the universality classes for various noninteracting surface reaction models. In Sec. III, the surface reaction models with lateral interactions are discussed. Finally, we summarize our discussions.

II Noninteracting surface reaction models

– Monomer-dimer model

In 1986, Ziff, Gulari and Barshad introduced a monomer-dimer(MD) model to describe the oxidation of carbon monoxide on a catalytic surface[26]. 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, composed of an O atom and a CO molecule, reacts and forms a CO_2 molecule and desorbs from the metal surface (Fig. 1). In two dimensions, as the CO gas pressure is lowered, the system undergoes a first-order transition from a CO-saturated inactive phase into a reactive phase and then a continuous transition into an O_2-saturated inactive phase. The O_2-saturated (absorbing) phase is not degenerate and the transition belongs to the DP universality class. In

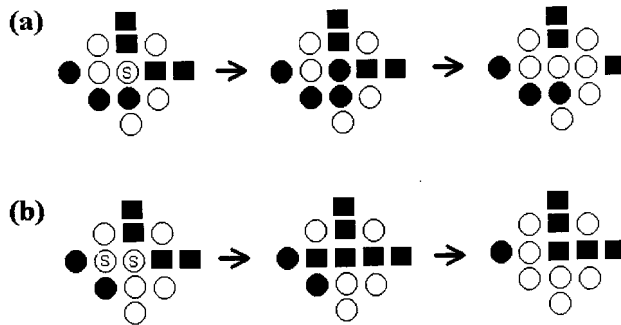one dimension, the MD model shows only a first-order transition between two saturated phases.

Figure 1. *Monomer-dimer model*: in (*a*), a CO molecule (filled circle) adsorbs on a selected empty site (open circle with S). The adsorbed CO molecule reacts with one of the nearest-neighbor O atoms (filled squares) and the resultant CO_2 molecule desorbs from the metal surface. In (*b*), an O_2 molecule adsorbs at a nearest-neighbor pair of vacant sites. These adsorbed O atoms react with one of nearest-neighbor CO molecule and the CO_2 molecule desorbs from the surface.

– *Monomer-monomer model*

Motivated by the MD model, various one-dimensional reaction models have been introduced to understand nonequilibrium dynamic critical behaviors. One simple example is the monomer-monomer(MM) model where particles of two different species, A and B, adsorb onto a single vacant site with probabilities p and $1 - p$ [28-30]. A nearest neighbor A-B pair of adsorbed particles reacts and desorbs from the lattice (Fig. 2). This model shows a first-order transition at $p = 1/2$ from the A-saturated phase into the B-saturated phase. Allowing desorption of one species(B), the MM model exhibits a continuous phase transition from the A-saturated phase into a reactive steady-state phase in one dimension [31, 32]. The A-saturated (absorbing) phase is not degenerate and this transition again belongs to DP universality class.
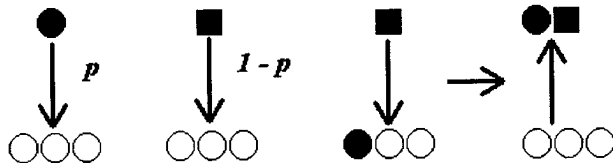

Figure 2. *Monomer-monomer model*: filled circles and filled squares represent A and B monomers respectively. A and B adsorb onto a single vacant site with probabilities p and $1 - p$, respectively. A nearest-neighbor A-B pair of adsorbed particles reacts and immediately desorbs from the surface.

– *Dimer-dimer model*

More complicated surface reaction models like the dimer-dimer(DD) model [33-35] and the dimer-trimer(DT) model [36, 37] have been also studied.

The DD model describes the oxidation of hydrogen molecules (H_2) on a metal surface. Both oxygen and hydrogen molecules adsorb onto a pair of adjacent vacant sites and then immediately dissociate. An adsorbed H diffuses and forms a OH molecule when it meets an O atom. A nearest neighbor OH - H pair reacts and forms an H_2O molecule and desorbs from the surface immediately. Spontaneous desorptions of a nearest-neighbor HH pair are also allowed. At the low H_2 pressure, the system gets into one of infinitely many absorbing states which is a mixture of O, OH, and single vacancies (Fig. 3). The number of absorbing states grows exponentially with system size and there is no clear-cut symmetry among absorbing states. Recently, it was argued that models with infinitely many absorbing states should belong to the DP class unless they possess any additional symmetry [38, 39]. Numerical simulations for the DD model and its variants show that the transition indeed belongs to the DP class. Many other complex models including the DT model possess infinitely many absorbing states and belong to the DP class [36, 37, 40].

Figure 3. A typical absorbing configuration of the DD model. V's, O's and H's correspond to vacant sites, oxygen atoms, and hydrogen atoms, respectively.

– *Three species monomer-monomer model*

Surface reaction models involving more than two species of particles have been also studied [18, 41, 42, 43]. Again, most of them belong to the DP class with infinitely many absorbing states except models with higher symmetry, for example, three species monomer-monomer model (3MM) introduced by Bassler and Browne [18]. In this model, three different but equivalent monomer species of particles (A, B, C) adsorb on single vacant sites with probabilities p_A, p_B, and p_C, such that $p_A + p_B + p_C = 1$. A nearest neighbor pair of dissimilar adsorbed monomers reacts and desorbs from the surface. When one species of monomers (e.g., C) is strongly suppressed with respect to the others ($p_C \ll p_A, p_B$), this model becomes similar to the MM model and shows a first order phase transition between the A-saturated phase and B-saturated phase at $p_A = p_B$ in one dimension. As p_C increases, a reactive phase appears through a continuous transition from the A-saturated (B-saturated) absorbing phase for $p_A > p_B$ ($p_B > p_A$). This continuous transition

also belongs to the DP class. However, along the symmetric line ($p_A = p_B$), there exist two equivalent absorbing states so the transition to the reactive phase through the bicritical point (the meeting point of two DP-type continuous transition lines) becomes of the DI type. $|p_A - p_B|$ plays a role of the symmetry breaking field discriminating the two absorbing states, which makes the system leave a DI fixed point and flow into a DP fixed point in the sense of a renormalization-group transformation [17, 44]. Similar bicritical points are found in some interacting reaction models (explained in the next section) and their critical behavior belongs to the DI class [19, 45, 46, 47].

III   Interacting surface reaction models

Lateral interactions between adsorbates in surface reaction models are often important in realistic physical and chemical adsorption problems [48, 49, 50, 51]. Especially nearest-neighbor excluded-volume type interactions may be interpreted as the effects of the reactant radius, which may be smaller or larger than the lattice spacing of adsorption sites. When the reactant radius is larger than the lattice spacing, lateral repulsive interactions significantly suppress the attempt to adsorb the particles in the nearest-neighbor vacant sites.

– *Interacting monomer-monomer model*

An interacting monomer-monomer model (IMM) has been introduced [46, 47] where monomers of the same species have variable lateral repulsive interactions in one dimension. In the IMM model, an A monomer can adsorb on a vacant site adjacent to an already-adsorbed A (restricted vacancy) with probability $r_A p_A$, where $0 \leq r_A \leq 1$. Similarly, B can adsorb on a restricted vacant site with probability $r_B p_B$. An A (B) monomer can adsorb on a free vacant site (no nearest-neighbor adsorbed monomers of the same type) with probability p_A (p_B). A nearest neighbor A-B pair of adsorbed particles reacts and desorbs from the lattice (Fig. 4). The limiting case $r_A = 0$ corresponds to the 'dollars and dimes' model [46], while the case $r_A = r_B = 1$ corresponds to the noninteracting MM model. When the interaction strength ($1-r_A$, $1-r_B$) is weak, the IMM model exhibits only a first-order phase transition between two saturated phases. At the critical value of the interaction strength, a first-order line terminates at a bicritical point beyond which two continuous DP type transition lines appear. The two saturated phases are separated from a reactive phase by these two lines. This feature in the phase diagram is

similar to the 3MM model discussed in the previous section. The bicritical behavior along the first-order line has been recently shown to belong to the DI universality class [19], due to equivalence of the two absorbing (saturated) states.
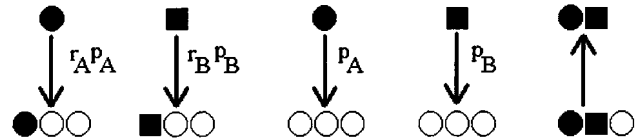

Figure 4. *Interacting monomer-monomer model*: open circles, filled circles and filled squares correspond to vacant sites, A, and B monomers respectively. A and B monomers adsorb onto restricted vacant sites with probabilities $r_A p_A$ and $r_B p_B$, respectively, and onto free vacant sites with p_A and p_B, respectively. A nearest-neighbor AB pair immediately desorbs from the surface.

– *Interacting monomer-dimer model*

Effects of lateral repulsive interactions in the MD model have been also studied intensively [15, 17, 21, 44, 49, 50, 51, 52]. As in the one-dimensional MM model, the first-order transition line between the two saturated phases bifurcates into two continuous DP-type transition lines with increasing interaction strength. Critical behavior at the bicritical point belongs to the DI class [45]. When the repulsive interactions between the same species of particles are infinitely strong, an interesting thing happens. A monomer (A) cannot adsorb at a restricted vacant site but adsorbs at a free vacant site (no adjacent monomer-occupied site) with probability p_A. Similarly, a dimer (B_2) cannot adsorb at a pair of restricted vacancies (B in neighboring sites) but adsorbs at a pair of free vacancies with probability p_B. A nearest neighbor of the adsorbed A and B reacts immediately, forms the AB product, and desorbs from the surface. Whenever there is an A adsorption attempt at a vacant site which neighbors an adsorbed A and B, we allow the A to adsorb and react immediately with the neighboring B (Fig. 5). (This is the crucial process to avoid infinitely many absorbing states, as will be discussed later.) Now the system has no fully saturated absorbing phases of monomers or dimers, but instead two equivalent half-filled absorbing states comprised of only monomers at alternating sites (odd-numbered or even-numbered lattice sites), i.e., ($A0A0\cdots$) and ($0A0A\cdots$) where '0' represents a vacancy. A dimer needs a pair of adjacent vacancies to adsorb, so these two states can be identified as the absorbing states. This IMD model exhibits a continuous transition from a reactive phase into the absorbing phase consisting of the two equivalent absorbing states.

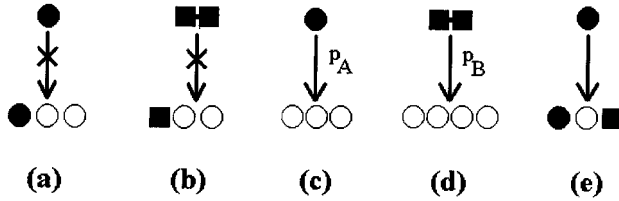This transition has been found to belong to the DI universality class.

Figure 5. *Interacting monomer-dimer model* : a monomer (filled circle) and dimer (filled square) adsorb at free empty sites with probabilities p_A and p_B, respectively. Neither species can adsorb at restricted vacant sites. Whenever there is a monomer-adsorption attempt at a vacant site which neighbors an adsorbed monomer and dimer, the monomer adsorbs and reacts immediately with the neighboring dimer.

In order to study the role of symmetry between the two absorbing states, a symmetry breaking field can be introduced, which favors one absorbing state over the other[17, 44, 52]. When a monomer is chosen to adsorb on an even-numbered free vacant site, the adsorption attempt is rejected with probability h. For finite h, the monomers tend to adsorb more on an odd-numbered site rather than an even-numbered one. Therefore, the absorbing state with monomers at odd-numbered sites can be reached more easily than the other absorbing state by the evolution dynamics. In fact, the ratio of the number of ensembles generated by static Monte Carlo simulations, falling into the disfavored absorbing state over that into the favored one, vanishes exponentially with system size at the transition point[17]. It implies that the chance of entering into the disfavored absorbing state is negligible in the thermodynamic limit, so the system behaves as if it had a single absorbing state, the favored one. So one can expect that the critical behavior at the absorbing transition should belong to the DP universality class. This has been confirmed in numerical simulations[17, 44].

– *Interacting monomer-trimer model*

In analogy to the IMM model, an interacting monomer-trimer model has been studied to investigate an absorbing transition with three equivalent absorbing states[53]. This may be viewed as a natural generalization in the quest for a new universality class, i.e., the directed version of the equilibrium 3-state Potts model. However, numerical study suggests that this model is always active, without a proper absorbing-state transition. None of the models studied so far with higher symmetries than the Ising symmetry has an absorbing transition[20, 53, 54]. A recent investigation of BAW-type models by Cardy and Täuber [25] may provide an

explanation for the absence of the absorbing phase in models with higher symmetries.

– *Interacting monomer-dimer model with infinitely many absorbing states*

An interesting variant of the IMD model has been introduced very recently [21]. This model possesses infinitely many absorbing (IMA) states with an extra global symmetry (Ising type) among absorbing states. The absorbing states can be divided into two equivalent groups. These two groups are dynamically separated infinitely far apart. In other words, an absorbing state in one group cannot be reached from any absorbing state in the other group by a finite number of successive local dynamic changes. This dynamic barrier is similar to the free energy barrier between ground states of equilibrium systems that exhibit spontaneous symmetry breaking in the ordered phase. Furthermore, there is a one-to-one mapping between the absorbing states in the two different groups. This ensures the Ising-type global symmetry in the system and the dynamic barrier causes the order-disorder-type absorbing transition.

The dynamic rules of this IMA-IMD model are almost the same as those of the IMD model with infinitely strong repulsion between the same species in one dimension. Differentiation between the IMA-IMD model and the ordinary IMD model comes in when there is a monomer (A) adsorption attempt at a vacant site between an adsorbed A and and an adsorbed B (Fig. 5(e)). In the IMA-IMD model, this process is disallowed. Then any configuration having neither nearest-neighbor pairs of vacancies nor single vacancies between two adsorbed B's is absorbing, for example, $(\cdots B0A0BB0A0A \cdots)$. To impose the Ising symmetry, spontaneous desorptions of a nearest-neighbor pair of adsorbed B's are allowed with probability s. For $s \neq 0$, an absorbing configuration cannot have this BB pair. Hence only those configurations that have particles at alternating sites and no two B's at consecutive alternating sites become absorbing states, e.g., $(A0A0B0A0 \cdots)$ and $(0A0A0B0A \cdots)$. So the absorbing states are divided into two equivalent groups with particles at odd- and even-numbered sites. The number of absorbing states grows exponentially with system size and it is clear that there is an Ising-type symmetry between these two groups. This model shows a continuous absorbing phase transition of the DI type.

When the desorption process of BB pairs is forbidden ($s = 0$), the system can find many more absorbing states with BB pairs as above, in addition to the two groups of the absorbing states. These new extra absorbing states are generically mixtures of these two groups, so they serve as a channel (or bridge) between the two

groups. Therefore there is no dynamic barrier between absorbing states any more and the system behaves like the other systems with infinitely many absorbing states without any extra symmetry. Numerical simulations confirm that the absorbing transition at $s = 0$ belongs to the DP universality class. Also, like in the IMD model with a symmetry breaking field, the system goes back to the DP class when the dynamic rules favor one group of absorbing states over the other.

IV   Summary

In summary, we surveyed various kinds of surface reaction models exhibiting absorbing phase transitions. Absorbing critical behaviors of all models studied thus far can be classified into two universality classes, i.e., the directed percolation (DP) and directed Ising (DI) classes. While the models with the two equivalent absorbing states or two equivalent groups of absorbing states belong to the DI universality class, the models with a single absorbing state or multiple absorbing states with one of them more prominent than the others belong to the DP universality class. These two universality classes are connected by the symmetry-breaking field which favors one absorbing state or group over the other one. Another scenario to move from the DI to DP class is to remove the dynamic barrier between the two groups of absorbing states.

Most of studies are done by numerical simulations, so a deeper understanding through analytic means is needed. Also various aspects like the dynamics of reaction fronts have to be investigated further in detail [6, 52, 55]. Recently, various multilayer versions of reaction models have been studied and their roughening and preroughening transitions found to be based on the DP-type and DI-type absorbing universality class [56-59]. Generalization of these models in this direction may be interesting. Another line of research should be a quest for a new universality class associated with higher symmetries.

Acknowledgments

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