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Rigorous Results on Mathematical Models of Catalytic Surfaces

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Two types of mathematical models of catalytic surfaces are considered. Conditions guaranteeing either convergence to traps with all sites occupied by a single reactant (poisoning) and or coexistence in equilibrium are established.

KEY WORDS: Catalytic surfaces; interacting particle systems; contact process.

1. INTRODUCTION AND RESULTS

1.1. Introduction

In this paper we examine a collection of interacting particle systems; we are motivated by the study of catalytic surface. Catalytic surfaces are substances composed of materials used to accelerate desirable chemical reactions which, in the absence of the catalyst, would proceed relatively slowly.[(1)] An example with practical applications is the platinum surface used to catalyze the reaction $2CO + O_2 \to 2CO_2$ (the motivation for accelerating the oxidation of carbon monoxide is clear in the context of automobile emissions). When a CO molecule lands on the surface, a single lattice site is occupied, while when an O_2 lands, it occupies a pair of sites. Denoting the state of adsorption onto the surface by *ads*, the reactions are

$$\begin{aligned} CO &\to CO(ads) \\ O_2 &\to 2O(ads) \\ CO(ads) + O(ads) &\to CO_2 \end{aligned} \tag{1}$$

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meaning that when a CO on the surface is near enough to an O, they react, forming a CO_2 molecule which diffuses from the surface. The system exhibits an interesting phase transition. If the partial pressure of CO is high enough relative to the O_2 pressure, the surface becomes covered by CO, and the reaction ceases, whereas for lower CO pressures, the reaction proceeds in equilibrium.

Numerous models of surface catalysts have been investigated.[2–6] An idealized description of the two-reactant system is as follows. The reactants, which we will call 1 and 2, diffuse in a gas above the surface. At certain rates the reactants bond to the surface, which we take to be a lattice. When two different reactants find themselves adjacent on the lattice, the activation energy for their usual reaction is lowered, and they react at a higher rate. The product of the reaction diffuses from the surface, vacating lattice sites. This idealization neglects diffusion on the surface, desorption of unreacted species, and the possibility that different species may occupy different types of lattice sites.

Such models of the catalyzed oxidation of CO are simulated in ref. 5 and a mean field description is examined numerically in ref. 2. It is found that for high concentrations (high landing rates) of either reactant relative to the other, the system "poisons"; that is, it hits a trap where the lattice is covered with one reactant. In this case, the reaction rate (the rate of production of the product CO_2) is zero. For intermediate concentrations, the coexistence of the two reactants on the surface is maintained, yielding a positive reaction rate in equilibrium. The bad news in this example is that the asymmetry in the occupation events, namely that the CO molecule requires a single vacant site to land, while the O_2 requires two adjacent vacant sites, makes rigorous analysis difficult.

In this paper we study several particle systems which, while devoid of this complicating asymmetry, do yield interesting and qualitatively similar behavior. The results are established for any dimension; however, the $d=2$ case is the one that the reader should associate with the standard catalytic surface. Next we describe the systems that we consider, along with the results proven. The proof of Theorem 1 is in Section 2.1, and the proof of Theorem 2(i) appears in Section 2.2. The proofs of Theorem 2(ii), (iii) are given in Section 2.3, and Section 2.4 contains the proof of Theorem 3.

1.2. The Systems Considered

The interacting particle systems which we consider have the state space $S^d(N)=\{0, 1, 2,..., N\}^{Z^d}$ with a given number of species N and dimension d. We will view sites in the lattice Z^d as vacant if a 0 is associated with a site, or as being occupied by species (molecule) i if an i

between 1 and N at the site. If we denote a configuration by η, then $\eta(x)$ will denote the state of site x in this configuration.

The systems have transition rates with the following general structure. First, to each species i, $1 \leqslant i \leqslant N$, is associated a landing rate p_i, which is the rate at which species i *attempts* to land at each site (i.e., the arrival times between attempted landings of species i at the sites are independent and exponentially distributed with parameter p_i). If the site is already occupied, nothing happens. The nontrivial interaction appears when we declare that certain species are not allowed to be adjacent to each other; if an attempted landing is made which would create a disallowed configuration, the landing individual and the discordant neighbor are instantly removed. This is the aspect which resembles catalytic surfaces—when two reacting species occupy adjacent sites, they react very rapidly (for our purposes instantly), forming another molecule which diffuses from the surface, freeing the previously occupied sites. We study two types of systems.

1.2.1. The Symmetric System. Here the rules are the following:

$$\begin{aligned} &0 \to i \text{ at rate } p_i \\ &ij \to 00 \text{ at rate } \infty \text{ if } i \neq 0,\ j \neq 0,\ i \neq j \end{aligned} \tag{2}$$

where ij denotes the occupation of two sites which are near neighbors. The p_i are normalized so that $\sum_i p_i = 1$. In all of the systems we discuss, if there is more than one neighbor with which a reaction could occur, a neighbor is selected with uniform probability among those possible. The presence of a rate taking the value ∞ is a notational luxury, which provides a concise way of stating a variety of rates. Alternatively, we could have enumerated the possible transitions (for instance, $102 \to 100$ at rate p_1, corresponding to attempted landings at the vacant site by species 1).

Note that there are N traps consisting of the point masses on configurations with all sites occupied by species i, $1 \leqslant i \leqslant N$, which we will denote by δ_i. When the system is in such a state, it is said to be "poisoned" and no reactions can occur.

1.2.2. The Asymmetric System. Here we consider only a two-species system with state space $S^d(2)$, where the usual interpretation of vacancy and occupation persists. The transition rates are

$$\begin{aligned} 0 &\to 1 \text{ at rate } p_1 \\ 0 &\to 2 \text{ at rate } p_2 \\ 12, 21, \text{ or } 22 &\to 00 \text{ at rate } \infty \end{aligned} \tag{3}$$

In this system species 2 reacts with itself as well as with species 1. Therefore, the only trap is δ_1. In a sense, species 1 has an advantage over species 2, since fewer occupation transitions are prohibited.

1.2.3. Remark on Construction. A graphical representation for any of the systems above can be constructed in the following manner: Picturing a temporal axis emanating from each site in Z^d, along each axis we deposit a sequence of $\bullet_i$'s as a Poisson process with parameter p_i for each species i: $1 \leqslant i \leqslant N$. Each $\bullet_i$ represents the (attempted) landing at the designated site by species i. If a $\bullet_i$ appears at a vacant site, and if no neighbors are occupied by species other than i, the site becomes occupied by species i. If neighbors exist which are occupied by another species, then one is selected randomly and vacated. A $\bullet_i$ landing at an occupied site does noting.

Note that the action of any $\bullet_i$ is confined to the designated site and its $2d$ neighbors. Two neighboring sizes x and y are said to be connected in the graphical representation in the time interval $[0, \tau]$ if a $\bullet_i$ occurred at one of the sites before τ. The construction of the process follows using a method due to Harris.[7] The idea is to select the time interval τ small enough so that with probability one all connected components of the graphical representation are finite. The process is then well defined on the initerval $[0, \tau]$, and the procedure can be iterated to construct the process for all time.

1.3. Results on the Symmetric System

The first result states that in any dimension, the only invariant measures in the two-species case ($N=2$) are the traps δ_1 and δ_2, except possibly at $p_1 = p_2 = 1/2$. The second result deals with a general number of species, and establishes conditions under which trapping (poisoning) or coexistence will occur in equilibrium.

Theorem 1. Consider the two-species system $N=2$ in any dimension. For $p_1 \neq 1/2$, the only invariant measures are linear combinations of δ_1 and δ_2.

Theorem 2. Consider the N-species symmetric system in any dimension starting from a nontrivial measure (one with support on configurations with an infinite number zeros).

(i) There exists an $\varepsilon_1 > 0$ so that if $p_i > 1 - \varepsilon_1$, then η_t converges in distribution to δ_i.

(ii) If $p_i < 1/(2d\lambda_c(d) + 1)$ [where $\lambda_c(d)$ is the critical value for the d-dimensional contact process; see Remark (d) below], then the system does not converge to δ_i.

(iii) There exists an integer N_d so that the number of species N exceeds N_d, then there exists an invariant measure with support on nontrivial configurations for values of $(p_1,..., p_N) \in C$, where C is a region of positive volume in $[0, 1]^d$. In other words, coexistence is possible in equilibrium.

Remarks. (a) Theorem 1 implies that coexistence in the two-species system in equilibrium is impossible, except possibly at the critical point $p_1 = p_2 = 1/2$.

(b) An examination of the proof of Theorem 1 shows that for any $N \geqslant 2$, if $p_i > 1/2$ for some i, then the only extremal invariant measures are the traps $\{\delta_i\}_{i=1}^N$. (In the proof give species i a charge of $+1$, and all other species -1.) This precludes coexistence in equilibrium.

(c) Part (ii) is used to obtain (iii) in the following way. If the number of species is selected large enough for a given dimension d, then each of the p_i can be selected so that $p_i < 1/2d\lambda_c(d) + 1$ under the constraint $\sum p_i = 1$. Coexistence occurs since the system can never reach any δ_i. For example, consider $d = 1$, where it is known rigorously[8] that $\lambda_c(1) < 2$. In this case if we choose $N \geqslant 5$, then coexistence can occur (take a neighborhood of the point $\{p_i = 1/N\}$).

(d) The contact process on Z^d is a stochastic growth model where each site is either occupied or vacant.[9,10] Occupied sites die (become vacant) at rate 1, and give birth at rate λ to each of their vacant neighbors. $\lambda_c(d)$ is the threshold below which the process becomes extinct and above which the system is supercritical.

1.4. Results on the Asymmetric System

Recall that the asymmetric system has only a single trap δ_1. Theorem 3 shows the existence of a phase transition in the asymmetric system, by establishing conditions under which the system traps and conditions for which coexistence occurs in equilibrium. This theorem is closely related to Theorem 2 for the N-species symmetric system, and in fact one can think of this system as the large-N limit of the symmetric system. To see this, consider the case where $p_2 = \cdots = p_N = (1 - p_1)/(N - 1)$, and group species 2,..., N together as a new species 2. When N is large, the rate of landing events which fill adjacent sites with the new species 2 is small.

Theorem 3. Consider the asymmetric system in any dimension with a nontrivial initial distribution.

(i) There exists an $\varepsilon_2 > 0$ so that if $p_1 > 1 - \varepsilon_2$, then the system converges to the trap δ_1.

(ii) If $p_1 < 1/2d\lambda_c(d) + 1$, then the system does not converge to δ_1, implying coexistence in equilibrium.

2. PROOFS OF THEOREMS

2.1. Proof of Theorem 1

Assume that $p_1 > 1/2 + \varepsilon$, for any $\varepsilon > 0$. Take a positive function $\alpha(x)$ such that $\sum_{x \in Z^d} \alpha(x) < \infty$. Consider the test function

$$Q = \sum_x \alpha(x)\, q[\eta(x)] \tag{4}$$

where

$$q(n) = \begin{cases} 1 & \text{if } n = 1 \\ 0 & \text{if } n = 0 \\ -1 & \text{if } n = 2 \end{cases} \tag{5}$$

We have given positive "charge" to species 1 and negative charge to species 2. If a 1 hits a vacant site x, Q changes by either $\alpha(x)$ or one of $\alpha(x \pm e_i)$, $i = 1,..., d$, where the e_i are unit vectors. Similarly, if a 2 lands at a vacant site, Q changes by $-\alpha(x)$ or $-\alpha(x \pm e_i)$. Define

$$\begin{aligned} \alpha_{\min}(x) &= \min(\alpha(x), \alpha(x \pm e_i)) \\ \alpha_{\max}(x) &= \max(\alpha(x), \alpha(x \pm e_i)) \\ \Delta(x) &= \alpha_{\max}(x) - \alpha_{\min}(x) \end{aligned} \tag{6}$$

We now see that

$$\begin{aligned} \frac{dE\{Q\}}{dt} &\geqslant E\left\{ \sum_x \left[p_1 \alpha_{\min}(x) - p_2 \alpha_{\max}(x) \right] 1_{\{\eta(x)=0\}} \right\} \\ &\geqslant \sum_x \left[-\tfrac{1}{2}\Delta(x) + 2\varepsilon \alpha_{\min}(x) \right] P(\eta(x) = 0) \end{aligned} \tag{7}$$

where $E(Q)$ denotes the expectation with respect to an invariant measure, and 1_A is the indicator function, which takes the value 1 when the event A occurs and zero otherwise. So, requiring $\Delta(x) < 4\varepsilon\alpha_{\min}(x)$ makes $dE\{Q\}/dt > 0$ unless the system is poisoned. It is easy to find an appropriate $\alpha(x)$. Take, for example,

$$\alpha(x) = e^{-\beta|x|}, \qquad \text{where} \quad \beta < \varepsilon \tag{8}$$

where $|x|$ is the L_1 norm. Since ε was arbitrary, we see that for any $p_1 > p_2$, no invariant measure has support on configurations with any 0's. Therefore, the only invariant measures are convex combinations of δ_1 and δ_2. The same result holds for $p_1 < p_2$ by symmetry.

2.2. Proof of Theorem 2, Part (i)

The goal is to show that if p_1 is chosen large enough, and if the system is started with a nontrivial initial distribution, then the distribution of the system converges to δ_1 almost surely. The plan is to construct a discrete-time set valued process which will function very much like the dual process for the biased voter model discussed in ref. 11, which essentially is treated like a random walk with drift. In our case the situation is considerably more unpleasant, since the nature of the dual process requires that we control a branching random walk. The tactic is to compensate for the branching mechanism by a strong drift toward the origin when p_1 is large.

2.2.1. A Result on Branching Random Walks. We begin by discussing a useful discrete-time branching random walk. At each time step, every particle is replaced by a set of particles. If a particle is at site x at time step n, then it is replaced at time step $n+1$ by the set $x+B$ with probability $P_x(B)$ (here $B \subset Z^d$ and $x+B$ is the translation of B by x). Our process will have the property that

$$\rho = \sum_{B \subset Z^d} |B| P_x(B) \tag{9}$$

is independent of x ($|B|$ denotes the cardinality of B).

Denote the configuration of this process starting from a single particle at x after n time steps by Z_n^x, and the number of particles at site y by $Z_n^x(y)$. Let $m(n, x, y) = E\{Z_n^x(y)\}$ and let S_n^x denote the random walk starting at x with transition density

$$p(x, x+y) = \frac{1}{\rho} \sum_{B \ni y} P_x(B) \tag{10}$$

The following result is used in the proof of Theorem 2(i).

Lemma 1. $m(n, x, y) = \rho^n P(S_n^x = y)$.

Proof. A property of the branching random walk is

$$m(n, x, y) = \sum_{B \subset Z^d} P_x(B) \sum_{z \in B} m(n-1, x+z, y) \tag{11}$$

Substituting the proposed solution into the right-hand side yields

$$\rho^{n-1}\sum_z\sum_{B\ni z} P_x(B)\,P(S_{n-1}^{x+z}=y)=\rho^n\sum_z \rho^{-1}\left[\sum_{B\ni z} P_x(B)\right]P(S_{n-1}^{x+z}=y)$$

$$=\rho^n\sum_z p(x,x+z)\,P(S_{n-1}^{x+z}=y)$$

$$=\rho^n P(S_n^x=y) \tag{12}$$

completing the proof.

2.2.2. The Dual Process. We begin with a few words of motivation. We want conditions on η_{n-1} which guarantee the presence of a 1 at site x and time n [i.e., $\eta_n(x)=1$]. We reverse time and discretize it into unit intervals denoted by $I_k=[k-1,k]$. In the original process this interval corresponds to times in $[n-k,\ n-k+1]$. We denote the landing of any species 2 to N by an $\times$. In one dimension, for example, suppose that during I_1, $\times$ landings occurred at $z+1$ and at $z+2$, but not at $z-1$ or at $z+3$. If we insist that 1's be at all three sites z, $z+1$, and $z+2$ at the end of I_1 [that is, $\eta_{n-1}(z)=\eta_{n-1}(z+1)=\eta_{n-1}(z+2)=1$], then we have guaranteed that $\eta_n(z)=1$. Similarly, suppose that at least two $\bullet_1$'s landed on site z during I_1. Further, suppose that *no* $\times$'s landed at site z or any of its neighbors during this interval. Then we could merely ask for a 1 at any single *neighbor* of z at the end of I_1, and this would guarantee that $\eta_n(z)=1$. We could select the neighboring site so that it is closer to the origin, and thus create a drift toward the origin in the dual process.

We will now make this precise. Associated with each site x and each time interval I_n are the following the following independent random variables. $\{T_i(x,n)\}_{i=1}^{2d}$ are exponentially distributed with parameter p_1. We let $S(x,n)=\sum_{i=1}^{2d} T_i(x,n)$. The S is supposed to be the time elapsed after $t=n-1$ until $2d$ $\bullet_1$ landing have occurred at site x. We let $U(x,n)$ be exponentially distributed with parameter $q=1-p_1$, denoting the time elapsed after $t=n-1$ until the first $\times$ landing at x.

Next we define the dual process starting at site x, which we denote by $\tilde{\eta}_n^x$. Suppose that $\tilde{\eta}_{n-1}^x=A\subset Z^d$. To find $\tilde{\eta}_n^x$, we perform two steps in order:

(i) Let $\Omega_n=\{z\colon U(z,n)<1\}$ be the set of all points which experienced an $\times$ landing during the time interval I_n. Let $\mathcal{N}_n(x,B)$ denote the following event: first, for all $y\in x+B$, $y\in\Omega_n$; second, there exists a nearest-neighbor path (in the site percolation sense) in Ω_n from y to any neighbor of x; and third, $\partial(x+B)\cap\Omega_n=\varnothing$ [where $\partial(R)$ denotes the boundary of R]. *The first step in determining* $\tilde{\eta}_n^x$ *is: for each* z, *if* $z\in\tilde{\eta}_{n-1}^x$ *and* $\mathcal{N}_n(z,B)$ *occurs, then replace* z *with* $z\cup B$.

(ii) $\mathscr{M}_n(z) = \{S(z, n) < 1 \text{ and } U(z, n) > 1\}$. For any site z, we select some (possibly random) subset $J(z)$ of its $2d$ neighbors and itself. *The second step is: if* $z \in \tilde{\eta}^x_{n-1}$ and $\mathscr{M}_n(z)$ *occurs, select* y *uniformly from* $J(z)$ *and replace* z *with* y. .

As discussed earlier, if $\tilde{\eta}^x_n$ hits only sites which are initially occupied by 1's, then $\eta(x) = 1$, because, as is easily checked, at each time step all unpleasant $\times$ landings are rendered harmless by the presence of a 1 at the target site. Therefore, we have the useful statement

$$P(\tilde{\eta}^x_n \subset A) \leqslant P(\eta^A_n(x) = 1) \tag{13}$$

where η^A denotes the system started with all sites in A occupied by 1's, and all other sites in any consistent configuration. When p_1 is large, the common events are the drift events in the second step, and the branching events in the first step are rare. This means that the particles drift toward the origin with an occasional branching event. Additionally, there is at most a single particle per site in the $\tilde{\eta}$ process, so that when events $\mathscr{N}$ or $\mathscr{M}$ at different sites place particles onto the same site, the particles coalesce.

2.2.3. A Branching Random Walk Upper Bound on $\tilde{\eta}$. In view of the preceding statements, we now define a process $\tilde{\zeta}^x$ which dominates the dual $\tilde{\eta}^x$, and in doing so we will describe a coupling between the two processes. First, define

$$H(z) = \{y: |y - z| = 1, \text{ and } \|y\|_2 < \|z\|_2, \text{ or } z_i = 0 \text{ and } y_i = 1\} \tag{14}$$

The rules of evolution are simply the rules described in the section preceding Lemma 1, where the offspring distribution is given by:

1. If $B = \{y\}$ with $y \in H(z) - z$, then $P_z(B) = (1/d)\, P(\mathscr{N}_n(z, \varnothing))\, P(\mathscr{M}_n(z))$.
2. If $B = \{0\}$, then $P_z(B) = P(\mathscr{N}_n(z, \varnothing))[1 - P(\mathscr{M}_n(z))]$
3. If $B = \{0\} \cup A$, $A \neq \varnothing$, then $P_z(B) = P_z(\mathscr{N}_n(z, A))$.
4. Otherwise, $P_z(B) = 0$.

Below the $\tilde{\zeta}^x$ process we will construct a version of the original $\tilde{\eta}^x$ process in such a way that $\tilde{\eta}^x_n(z) = 1 \Rightarrow \tilde{\zeta}^x_n(z) \geqslant 1$. To do this, we first note that one way to construct the branching random walk $\tilde{\zeta}^x$ is to associate with each particle in $\tilde{\zeta}^x$ its own set of independent random variables analogous to $S(x, n)$ and $U(x, n)$ in the $\tilde{\eta}^x$ process.

We index particles at time n by L_n: $1 \leqslant L_n \leqslant N_n$, where N_n is the number of particles at time n. Recall that if a particle at site x at time $n-1$ is replaced by the set $\{x\}$ at time n, we think of this occupying particle as

being an offspring even though it occupies the same site as the parent; so all particles at time n are in the nth generation. Also, let x_{L_n} be the position of particle L_n. For particle L_n, let $\{T_i^{L_n}\}_{i=1}^{2d}$ be independent exponential random variables with parameter p_1, and $S^{L_n} = \sum_{i=1}^{2d} T_i^{L_n}$. Let $U^{L_n}(z)$ be exponential with parameter $q = 1 - p_1$ for all $z \in Z^d$.

(i) Let $\Omega_{L_n} = \{z: U^{L_n}(z) < 1\}$, denoting those sites for which U^{L_n} occurred before time 1. Let $\mathscr{B}_{L_n}$ be

$$\mathscr{B}_{L_n} = x_{L_n} \cup \{z: z \to \text{nbr}(x_{L_n}) \text{ in } \Omega_{L_n}\} \tag{15}$$

where $\text{nbr}(x)$ denotes the $2d$ nearest neighbors of site x. Add one particle to each site in $\mathscr{B}_{L_n}$ for each L_n.

(ii) Let $\mathscr{M}_{L_n} = \{S^{L_n} < 1,\ U^{L_n} > 1\}$. If $\mathscr{M}_{L_n}$ occurs, select a neighboring site z from $H(x_{L_n})$ and replace x_{L_n} with z.

This constructs $\tilde{\zeta}^x$. We proceed to construct $\tilde{\eta}^x$. Our goal is to assign random variables $S(x, n)$ and $U(x, n)$ for each $x \in Z^d$. In particular, we will want to know $\Omega_n = \{x:\ U(x, n) < 1\}$. To do this, we enumerate the following steps.

1. Order the particles in $\tilde{\eta}_{n-1}^x$ by location lexicographically. Denote this ordering by $\{x_1, \ldots, x_{N_{n-1}}\}$.

2. At each x_i order the particles in $\tilde{\zeta}_{n-1}^x(x_i)$ according to lexicographic order of the parents (then the grandparents, etc.). Let e_i denote the lowest.

3. Starting with the particle at x_1, consider Ω_{e_1} and $\mathscr{B}_{e_1}$ in the $\tilde{\zeta}^x$ construction. We declare that:

(A) $\Omega_n \supseteq \mathscr{B}_{e_1}$

(B) $\Omega_n \cap \partial(\mathscr{B}_{e_1}) = \varnothing$

4. Iterate through the set $\{x_1, \ldots, x_{N_{n-1}}\}$, using, instead of $\mathscr{B}_{e_i}$, the set

$$C_{e_i} = \mathscr{B}_{e_i} \Bigg\backslash \left\{ \mathscr{B}_{e_i} \cap \left[\bigcup_{k=1}^{i-1} \mathscr{B}_{e_k} \bigcup_{k=1}^{i-1} \partial(\mathscr{B}_{e_k}) \right] \right\} \tag{16}$$

In this way we never interfere with previously assigned events (times).

5. Fill all sites in $\bigcup_i C_{e_i}$ with 1's.

6. Assign all other $U(z, n)$'s i.i.d. exponential with parameter q, and assign $S(z, n)$ by S^{e_i} if $z = x_i$ for some i, or i.i.d. as before.

7. Let $\mathscr{M}_{e_i} = \{S^{e_i} < 1,\ U^{e_i} > 1\}$. If $\mathscr{M}_{e_i} \cap \{\mathscr{B}_{e_i} = \{x_i\}\}$ occurs, replace x_i with a site z chosen uniformly from $H(x_i)$. Note that if $U(x_i, n) < 1$, we still have x_i occupied at time n.

8. If $\mathscr{M}_{e_i} \cap \{\mathscr{B}_{e_i} = \{x_i\}\}$ does not occur, but $\{U(x_i, n) > 1\}$, then let $J(x_i) = \{x_i\}$ in step (ii) of the construction of η.

This constructs $\tilde{\eta}^x \leqslant \tilde{\zeta}^x$.

We now make a statement regarding bounds on the maximum possible jump size of the associated random walk S_n^x.

Lemma 2. We have

$$P(|S_n^x - S_{n-1}^x| \geqslant L) \leqslant C \exp\left\{-L \log\left[\frac{1}{(2d-1)\hat{q}}\right]\right\} \tag{17}$$

where $\hat{q} = 1 - e^{-q}$ (where $q = 1 - p_1$ is the cumulative landing rate of species 2 through N).

Proof. From examination of the transition density, the probability that the jump size exceeds L is bounded above by the probability that there exists a self-avoiding path of length L from the origin in the associated Bernoulli site percolation problem with occupation density $\hat{q}$. This is bounded above (using standard counting methods) by

$$d(2d-1)^{L-1}\hat{q}^L \tag{18}$$

which implies the desired result.

2.2.4. The Renormalization Scheme. The goal is to show that if the system finds that it has filled some large box with 1's, then with probability close to one it will fill an infinite sequence of boxes with exponentially growing dimension. To make this precise, for some presently unspecified β and μ, define

$$\beta_k = 2^k \beta, \qquad s_k = \frac{\beta_k}{\mu} \tag{19}$$

and let $R_k = \{x: \|x\|_2 \leqslant \beta_k\}$. It is presumed that β and μ are selected so that the above quantities are integers. The s_k represent time increments, so that the real time elapsed through level k is $t_k = s_1 + \cdots + s_k$. The proof of Theorem 2(i) will be complete upon showing the following.

Lemma 3. There exist numbers $p_k(\beta)$ with $\sum_{k=1}^{\infty} p_k(\beta) \to 0$ as $\beta \to \infty$, and a value of μ so that

$$P(\eta_t^{R_{k-1}} \not\supset R_k \text{ for some } t \in [s_k, s_k + s_{k+1}]) \leqslant p_k(\beta) \tag{20}$$

Proof. We begin by using the dual process. Recall that η^A denotes the system started with A occupied by 1's, and $\tilde{\zeta}_n^x(A)$ denote the number of

particles in the branching random walk in set A at time n, starting from a single particle at x. We know that for any $x \in R_k$ and any integer n

$$\begin{aligned} P(x \notin \eta_n^{R_{k-1}}) &\leqslant P(\tilde{\eta}_n^x \cap R_{k-1}^c \neq \varnothing) \\ &\leqslant E\{\tilde{\zeta}_n^x(R_{k-1}^c)\} \\ &= \rho^n P(S_n^x \in R_{k-1}^c) \end{aligned} \tag{21}$$

where the last step followed by Lemma 1. We first show that if p_1 is large, then for large n, the probability that S_n^x is farther than R from the origin dies exponentially in R.

Lemma 4. Consider a discrete-time process starting at α, denoted by Z_n^α. Suppose that, for some $\kappa > 0$:

(i) $P(|Z_{n+1}^\alpha - Z_n^\alpha| \geqslant L) \leqslant Ce^{-\kappa L}$

(ii) $E\{Z_{n+1}^\alpha - Z_n^\alpha | \mathscr{F}_n\} \leqslant -v - \varepsilon$ when $Z_n^\alpha \geqslant 0$ ($\mathscr{F}_n$ is the filtration up to time n). Then,

$$P(Z_n^\alpha \geqslant y) \leqslant Ke^{-\delta y}[1 + e^{-\delta(vn/2 - \alpha)}] \tag{22}$$

where K and δ depend only on ε, v, C, α, and κ.

Proof. It is sufficient to show

$$E\{e^{\delta Z_n^\alpha}\} \leqslant C_\delta[1 + e^{-\delta(vn/2 - \alpha)}] \tag{23}$$

since by Chebyshev's inequality we have

$$P(Z_n^\alpha \geqslant y) = P(e^{\delta Z_n^\alpha} \geqslant e^{\delta y}) \leqslant e^{-\delta y} E\{e^{\delta Z_n^\alpha}\} \tag{24}$$

In turn, to show (23), it is sufficient to show

$$E\{e^{\delta Z_{n+1}^\alpha}\} \leqslant (1 - \delta v)\, E\{e^{\delta Z_n^\alpha}\} + \delta v + M \tag{25}$$

for some constant M. It is easy to check that (25) implies that for small δ

$$\begin{aligned} E\{e^{\delta Z_n^\alpha}\} &\leqslant (1 - \delta v)^n\, E\{e^{\delta Z_0^\alpha}\} + \frac{\delta v + M}{\delta v}[1 - (1 - \delta v)^n] \\ &\leqslant e^{[n \log(1 - \delta v) + \delta\alpha]} + \frac{\delta v + M}{\delta v} \end{aligned} \tag{26}$$

where we used the fact that $A_0^\alpha = \alpha$. Finally, linearizing the logarithm for small δ yields the desired result if C_δ is large enough.

We now establish (25). We have

$$E\{e^{\delta Z_{n+1}^{\alpha}} - e^{\delta Z_n^{\alpha}}\} = E\{e^{\delta Z_n^{\alpha}}[e^{\delta(Z_{n+1}^{\alpha} - Z_n^{\alpha})} - 1]\}$$
$$= E\{e^{\delta Z_n^{\alpha}} E\{e^{\delta(Z_{n+1}^{\alpha} - Z_n^{\alpha})} - 1 \mid \mathscr{F}_n\}\} \tag{27}$$

On $\{Z_n^{\alpha} \geqslant 0\}$, when δ is small [linearizing the exponent and comparing to (ii)], we have

$$E\{e^{\delta(Z_{n+1}^{\alpha} - Z_n^{\alpha})} - 1 \mid \mathscr{F}_n\} \leqslant -\delta v \tag{28}$$

Finally, on $\{Z_n^{\alpha} < 0\}$, (i) yields

$$E\{e^{\delta(Z_{n+1}^{\alpha} - Z_n^{\alpha})} - 1\} \leqslant \int_L^{\infty} e^{\delta y} C e^{-\kappa y}\, dy = M < \infty \tag{29}$$

for small δ. Putting this all together, we have that the right-hand side of (27) is bounded by

$$E\{e^{\delta Z_n^{\alpha}}[-\delta v 1_{\{Z_n^{\alpha} \in [0, +\infty)\}} + M 1_{\{Z_n^{\alpha} \in (-\infty, 0)\}}]\}$$
$$\leqslant E\{-\delta v e^{\delta Z_n^{\alpha}} + (\delta v + M) 1_{\{Z_n^{\alpha} \in (-\infty, 0)\}}\}$$
$$\leqslant -\delta v E\{e^{\delta Z_n^{\alpha}}\} + \delta v + M \tag{30}$$

where we have used

$$E\{e^{\delta Z_n^{\alpha}} 1_{\{Z_n^{\alpha} \in (-\infty, 0)\}}\} \leqslant 1 \tag{31}$$

This completes the proof of Lemma 4.

Before establishing Lemma 3, and therefore Theorem 2(i), we will use Lemma 4 to bound the probability that S_n^x is far away from the origin.

Lemma 5. Let $Z_n^{\alpha} = \|S_n^x\|_2 - \gamma$, with $\alpha = \|x\|_2 - \gamma$.

(i) If γ is large enough, then for some $\varepsilon > 0$, then there exists a $\theta > 0$ so that if $p_1 > 1 - \theta$, then

$$E\{Z_{n+1}^{\alpha} - Z_n^{\alpha} \mid \mathscr{F}_n\} \leqslant -v - \varepsilon \tag{32}$$

on $\{Z_n^{\alpha} \geqslant 0\}$, where $v = c/d$, some $c > 0$.

(ii) For any $\sigma > 0$, there exists a $\phi > 0$ so that if $p_1 > 1 - \phi$, then $\rho < 1 + \sigma$.

Proof. The proof of (i) is very similar to the corresponding statement in ref. 11. In particular, the drift toward the origin is minimized when the

random walk is on one of the axes. When γ is large, this drift is asymptotically

$$-\frac{1}{d}P(S(x,n)<1,\ U(z,n)>1\ \forall z:\ |z-x|\leqslant 1)+C\int_0^\infty Le^{-\kappa L}\,dL \quad (33)$$

where

$$\kappa=\log\frac{1}{(2d-1)(1-e^{-(1-p_1)})} \quad (34)$$

If p_1 is close enough to 1, the first term exceeds the second, implying the result.

The proof of (ii) is even easier, since the expected cluster size in site percolation diminishes to zero as occupation probability vanishes. Therefore, as p_1 increases to one, the mass is moved to sets B with $|B|=1$, and $\rho\to 1$.

We now prove Lemma 3. For any $x\in R_k$ and any integer $n\in[s_k, s_k+s_{k+1}]$ we have

$$P(x\notin\eta_n^{R_{k-1}})\leqslant\rho^{(s_k+s_{k+1})}P(S_n^x\in R_{k-1}^c) \quad (35)$$

We bound the first term on the right:

$$\begin{aligned}\rho^{(s_k+s_{k+1})}&\leqslant(1+\sigma)^{(2^k+2^{k+1})\beta/\mu}=(1+\sigma)^{(3\beta/\mu)2^k}\\&=\exp\left\{\beta 2^k\left[\frac{3}{\mu}\log(1+\sigma)\right]\right\}\end{aligned} \quad (36)$$

Next we bound

$$\begin{aligned}p(S_n^x\in R_{k-1}^c)&=p(\|S_n^x\|_2>2^{k-1}\beta)\\&\leqslant P(Z_n^\alpha>2^{k-1}\beta-\gamma)\\&\leqslant K\exp\left(\delta\frac{2^{k-1}\beta}{2}\right)\left\{1+\exp\left[-\delta\left(\frac{1}{2}\nu n-\beta_k+\gamma\right)\right]\right\}\\&\leqslant K\exp(-\delta 2^{k-2}\beta)\left\{1+\exp\left[-\delta\left(\frac{1}{2}\nu\frac{2^k\beta}{\mu}-2^k\beta\right)\right]\right\}\end{aligned} \quad (37)$$

where we have taken γ large enough to use Lemma 5, and then set $\beta>2\gamma$. In using these results, we have taken δ positive, but as small as necessary. We can now reduce μ so the the second exponent in the last line is negative. Finally, we can take σ small (by making p_1 large), so that the right-hand side of (35) is decaying exponentially in k and in β as

$$P(x\notin\eta_n^{R_{k-1}})\leqslant 2Ke^{-\beta 2^{k-2}\delta/2}=2Ke^{-\beta 2^{k-3}\delta} \quad (38)$$

It is clear that a trivial modification in the first step of the dual process $\tilde{\eta}^x$ and the dominating $\tilde{\zeta}^x$ process yields this bound for any real $t \in [s_k, s_k + s_{k+1}]$.

We need to show that if β is large enough, then with high probability *all* sites in R_k are occupied for *all* $t \in [s_k, s_k + s_{k+1}]$ starting from R_{k-1}. Note that if $x \notin \eta_t^{R_{k-1}}$, then with probability exceeding e^{-p_1}, x remains unoccupied by a 1 during $[t, t+1]$. Using this fact, and letting $|I|$ denote the Lebesque measure of a set I, then for any $x \in R_k$,

$$\begin{aligned} &P(x \notin \eta_t^{R_{k-1}} \text{ some } t \in [s_k, s_k + s_{k+1}])e^{-p_1} \\ &\quad \leqslant E\{|\{t \in [s_k, s_k + s_{k+1} + 1]: x \notin \eta_t^{R_{k-1}}\}|\} \\ &\quad \leqslant 2K(1 + s_{k+1})e^{-2^{k-3}\beta\delta} \end{aligned} \tag{39}$$

Consequently,

$$P(\eta_t^{R_{k-1}} \not\supset R_k \text{ some } t \in [s_k, s_k + s_{k+1}]) \leqslant 2|R_k| e^{p_1} K(1 + s_{k+1})e^{-2^{k-3}\beta\delta} \tag{40}$$

which establishes the existence of the desired $p_k(\beta)$, upon noting that the exponential growth of $|R_k|(1 + s_{k+1})$ is much slower than the super-exponential decay of $\exp(-2^{k-3}\beta\delta)$. This completes the proof of Lemma 3, and of Theorem 2(i).

2.3. Proof of Theorem 2, Parts (ii) and (iii)

Proof of Theorem 2, (ii) (take $i = 1$ for definiteness). We will show that species 1 does not poison the system, by a coupling argument with a contact process. Notation is as follows: configuration of the N species system will be denoted by $\eta \in S^d(N)$, those of a recoding of this system (to be described) are $\zeta \in \{0, 1\}^{Z^d}$, and those of the contact process are $\xi \in \{0, 1\}^{Z^d}$.

The first step is to map any configuration η into a configuration ζ:

$$\zeta(x) = f[\eta(x)] \qquad \text{where} \quad f(i) = \begin{cases} 0 & \text{if } i = 1 \\ 1 & \text{if } i = 0 \text{ or } 2 \leqslant i \leqslant N \end{cases} \tag{41}$$

Thus, a site in ζ is considered to be occupied if the same site in η is occupied by any of species 2 through N or if it is vacant. If species 1 occupies the site in η, then the corresponding site in ζ is vacant. It is also worth noting that if a 1 is next to a 0 in the ζ process, then the 1 must represent a 0 in the original η process.

The next step is to construct a graphical representation for the evolu-

tion of the recoded process ζ, derived from the rates which prescribe the evolution of the original process η. We use the graphical representation described in Section 1.2. We will write the $\bullet_1$'s as $\times$'s, however, to distinguish their effects.

This graphical representation is a way of viewing the evolution of the N-species system. The recoding through f induces an evolution of the ζ configuration. In the recoded process, 1's give birth onto 0's at a rate of *at least* $(p_2 + \cdots + p_N)/2d$, which corresponds to the worst case of a vacant site in the original process with all neighbors occupied by species 1. Additionally, $\times$ marks turn 1's in ζ into 0's only if the recoded 1 corresponded to a 0 with all neighbors either vacant or occupied by species 1. Consequently, the *maximum* rate at which 1's turn to 0's in the ζ process is p_1.

Furthermore, and of primary importance, the graphical representation induces a coupling between the evolution of a contact process ξ and the recoded system ζ in such a way that if $\zeta_0(x) \geqslant \xi_0(x)$ for all x, then $\zeta_t(x) \geqslant \xi_t(x)$ for all x at all subsequent times $t > 0$. In the contact process ξ, we prescribe that $\times$'s turn 1's into 0's, and any $\bullet_i$ that hits a 1 turns a randomly selected neighbor into a 1 (if it was not already a 1). This contact process has death rate p_1, and birth rate $(p_2 + \cdots + p_N)/2d = (1 - p_1)/2d$ to each neighbor. It can be explicitly checked (there are only five possibilities) that no transitions are possible from a configuration in which $\zeta \geqslant \xi$ that would create a site x at which $\zeta(x) = 0$ and $\xi(x) = 1$.

Therefore, if the ratio of the birth rate to the death rate exceeds $\lambda_c(d)$, then the contact process ξ is supercritical, implying that the ζ process is also supercritical. Recalling the mapping $f: \eta \to \zeta$, this means that when we start with a nontrivial initial distribution (i.e., with an infinite number of 0's in the original η process), then there are always sites occupied by $\{0, 2, 3, 4, \ldots, N-1\}$, implying that the system cannot trap to δ_1 (see ref. 10 or ref. 9).

Part (iii). Since $\lambda_c(d) < \infty$ (and is, in fact, nonincreasing in d), there exists an integer N_d so that the set of solutions of

$$p_i \leqslant \frac{1}{2d\lambda_c(d) + 1} \quad \forall i, \qquad \sum p_i = 1 \tag{42}$$

is a neighborhood of the point $\{p_i = 1/N\}$. In this neighborhood, by the proof of (ii), if we group any $N-1$ of the N species together with 0's, calling this resulting group species A, this process dominates a supercritical contact process. Now start the system with a nontrivial translation-invariant measure μ and with the values of the p_i selected in the neighborhood described above.

The process η_t is clearly Feller, and the state space $\{0, 1,..., N\}^{Z^d}$ is compact. Therefore, denoting the semigroup of η_t by $S(t)$, we have that the Cesaro average $(1/T)\int_0^T \mu S(t)\, dt$ converges along some subsequence $\{T_n\}_{n=1}^{\infty}$ with $T_n \to \infty$ as $n \to \infty$. The limit is an invariant measure (see ref. 9), which we will denote by ν. Let

$$\begin{aligned} I &= \{\eta \in S^d(N): |x: \eta(x) = 0| = \infty\} \\ F &= \{\eta \in S^d(N): 0 < |x: \eta(x) = 0| < \infty\} \\ Z &= \{\eta \in S^d(N): |x: \eta(x) = 0| = 0\} \end{aligned} \tag{43}$$

Now, $\nu(F) = 0$ by translation invariance. Additionally, configurations on Z consist of $\{\eta: \eta(x) = i\ \forall x\}$ for some $1 \leqslant i \leqslant N$. Therefore, $\nu(\cdot \mid Z) = \sum_{i=1}^{N} c_i \delta_i$ with $c_i \geqslant 0$ and $c_j > 0$ for some j unless $\nu(Z) = 0$. Assuming that $\nu(Z) > 0$ and, without loss of generality, that $c_1 > 0$, then

$$\nu(\delta_1) \geqslant c_1 \nu(Z) \tag{44}$$

However, if we let $A = \{0, 2, 3,..., N\}$, we know by comparison with the associated supercritical contact process that $\nu(\delta_1) = 0$, contradicting the assumption that $\nu(Z) > 0$.

We are left, therefore, with the conclusion that the support of ν is I, the set of nontrivial configurations.

2.4. Proof of Theorem 3

The proofs of the two parts of Theorem 3 are essentially identical to those of the corresponding part of Theorem 2.

Part (i). This follows directly from the argument used in the proof of Theorem 2(i).

Part (ii). Here, as before, we couple the system to a contact process. In this case we consider to 0's and 2's to be alive and the 1's to be dead. We will denote a configuration of the original asymmetric process η, of the recoded process ζ, and of the contact process by ξ. We see that

$$\zeta(x) = \begin{cases} 1 & \text{if } \eta(x) = 0, 2 \\ 0 & \text{if } \eta(x) = 1 \end{cases} \tag{45}$$

Now consider a graphical representation which couples the asymmetric process to the contact process, where a $\times$ represents the arrival of a 1 for the catalyst and a death mark for the contact process. A $\bullet$ represents the arrival of a 2 for the catalyst and a birth mark for the contact process.

Birth marks behave identically in the two systems: if you are already alive you stay alive, and if there are dead sites adjacent to you, you select one at random which becomes alive. Death marks, however, can behave differently. If a death mark hits a 2, it does not die, and if it hits a 0 that a adjacent to a 2, the 0 will not die.

Using this coupling, and denoting configurations at time t, by a subscript t, we see that if initially $\zeta_0(x) \geq \xi_0(x)$, then $\zeta_t(x) \geq \xi_t(x)$ for all $t > 0$. Then the rest of the proof goes through as before. We get the same bound, that is, if $p_2/2dp_1 > \lambda_c(d)$, then the contact process ξ is supercritical, and therefore the ζ process is, too, implying that 2's and 0's persist. Noting that $p_2 = 1 - p_1$ completes the proof.

2.5. Conclusions

We have examined two types of models of surface catalysts, and we have shown that under certain conditions these idealizations exhibit both types of behavior found in real systems. Namely, if a single species lands at a high rate, the system will trap to a configuration with all sites occupied by that species, whereas if the landing rates are comparable, then coexistence in equilibrium occurs.

A limitation of these results is that the landing events involve the vacancy of a single site. In these models there is no coexistence in the physically most relevant two-species symmetric system. To prove coexistence, we must either resort to a fairly large number of species (that is, five), or require that one species interact with itself. (We should perhaps note that we have performed computer simulations which show that five species is not a strict bound. Even the $N = 3$ symmetric case can show coexistence if the p_i are chosen within about 0.1 of 1/3.) It seems clear that some asymmetry is necessary for a two-component system to show coexistence in equilibrium, and a desired improvement would be to show coexistence in a less artificial two-component system, perhaps the CO, O_2 model described in the Introduction.

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