

## Kinetics of catalysis with surface disorder

D. A. Head\* and G. J. Rodgers

Department of Physics, Brunel University, Uxbridge, Middlesex, UB8 3PH, United Kingdom

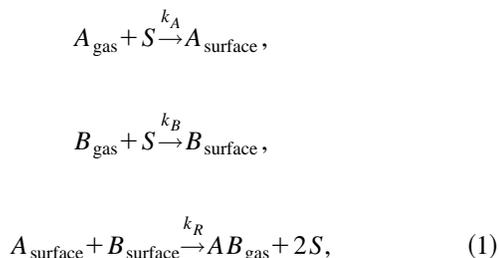
(Received 20 February 1996)

We study the effects of generalized surface disorder on the monomer-monomer model of heterogeneous catalysis, where disorder is implemented by allowing different adsorption rates for each lattice site. By mapping the system in the reaction-controlled limit onto a kinetic Ising model, we derive the rate equations for the one- and two-spin correlation functions. There is good agreement between these equations and numerical simulations. We then study the inclusion of desorption of monomers from the substrate, first by both species and then by just one, and find exact time-dependent solutions for the one-spin correlation functions. [S1063-651X(96)01708-4]

PACS number(s): 05.70.Ln, 82.65.Jv, 82.20.Mj

### I. INTRODUCTION

Diffusionless surface-reaction models were first introduced by Ziff, Gulari, and Barshad [1], who investigated a monomer-dimer reaction corresponding to the chemical reaction  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$  on a catalytic surface. A well-studied variant [2–4] employs the simpler monomer-monomer reaction, described by



where  $S$  denotes an empty site. This process exhibits a *kinetic phase* when there are equal propensities of  $A$  and  $B$  species, in which the long-time kinetics become dominated by domain coarsening. Mean-field analysis [5], in which every site is taken to be connected to every other site in a ‘‘complete graph,’’ demonstrated that finite lattices will always saturate—that is, the lattice will either become full of  $A$ 's, or full of  $B$ 's, and the process will stop. Krapivsky [6] recently solved the model exactly in the reaction-controlled limit  $k_R \rightarrow \infty$  by mapping the system onto the standard Ising model.

Many enhancements to these models have been studied with a view to more closely modeling actual chemical processes, including nearest-neighbor excluded adsorption [7] and surface diffusion [4,8]. However, only recently have the effects of surface disorder been touched upon by Frachebourg *et al.* [9]. They chose to model a disordered surface by taking a lattice of two different types of site, one that favors

adsorption by the  $A$  species and one which favors adsorption by the  $B$ 's. They showed numerically that such disorder allows for a reactive equilibrium in two dimensions.

In this paper, we extend the analytical method used in [6] to a general form of surface disorder, based on [9] but allowing for a range of different types of site in the lattice. Furthermore, we also investigate separately the effects of desorption in the system. All the results presented are for the physically relevant case of two dimensions.

This paper is organized as follows. In Sec. II we define the model and derive the general rate equations for the  $n$ -spin correlation functions. In Sec. III, these equations are applied to a model similar to that in [9] and their solutions are compared to numerical simulations. In Secs. IV and V we include the effects of desorption, first by both species and then by just one, and derive exact solutions. The conclusions are summarized in Sec. VI.

### II. RATE EQUATIONS

We consider the surface reaction  $A + B \rightarrow 2S$  on a periodic  $L \times L$  square lattice, ignoring the effects of diffusion and desorption. For simplicity, we take the reaction-controlled limit, where the adsorption of  $A$  and  $B$  species is taken to be infinitely fast so that the substrate is always full. The algorithm employed here is to select a nearest-neighbor (NN) pair at random, check for an  $AB$  reaction, and, if so, remove the particles and immediately refill both sites.

With the usual homogeneous model, the probability of filling a site with an  $A$  or  $B$  is independent of the site chosen—in this model, however, that probability is allowed to vary. Specifically, we introduce the *site inhomogeneity* matrix  $P_{ij}$ ,  $0 \leq P_{ij} \leq 1 \forall i, j$ , such that the probability of filling the site  $(i, j)$  with an  $A$  is given by  $P_{ij}$  (or, equivalently, a probability  $1 - P_{ij}$  of filling the site with a  $B$ ).

Since in the reaction-controlled limit each site  $(i, j)$  has only two possible states, we can map this model onto an Ising model with mixed Glauber-Kawasaki dynamics [6], identifying  $A$ 's with  $S_{ij} = +1$  and  $B$ 's with  $S_{ij} = -1$ . The master equation for  $P(S, t)$ , the probability distribution for the system to be in the state  $S = \{S_{ij}\}$  at time  $t$ , is

\*Electronic address: David.Head@brunel.ac.uk

$$\begin{aligned}
\frac{d}{dt} P(S,t) = & \sum_{i,j} [U_{ij}(F_{ij}S)P(F_{ij}S,t) - U_{ij}(S)P(S,t)] \\
& + \sum_{i,j} [V_{ij}(F_{ij}F_{i+1}S)P(F_{ij}F_{i+1}S,t) \\
& - V_{ij}(S)P(S,t)] \\
& + \sum_{i,j} [W_{ij}(F_{ij}F_{ij+1}S)P(F_{ij}F_{ij+1}S,t) \\
& - W_{ij}(S)P(S,t)]. \tag{2}
\end{aligned}$$

The flip operator  $F_{ij}$  acts on the system-state vector  $S$  by flipping the sign of the  $S_{ij}$  component, leaving the remaining components unchanged.  $U_{ij}$  corresponds to Glauber spin-flip dynamics [10], whereas  $V_{ij}$  and  $W_{ij}$  correspond to Kawasaki exchange dynamics. Equation (2) is identical to the homogeneous case, except that now the full expressions for  $U_{ij}$ ,  $V_{ij}$ , and  $W_{ij}$  are given by

$$\begin{aligned}
4\tau_1 U_{ij} = & (1 - S_{ij}S_{i+1})\{1 - d_{ij} + S_{ij}(1 - a_{ij}^+)\} \\
& + (1 - S_{ij}S_{i-1})\{1 - d_{i-1j} + S_{ij}(1 - a_{i-1j}^+)\} \\
& + (1 - S_{ij}S_{ij+1})\{1 - e_{ij} + S_{ij}(1 - b_{ij}^+)\} \\
& + (1 - S_{ij}S_{ij-1})\{1 - e_{ij-1} + S_{ij}(1 - b_{ij-1}^+)\}, \tag{3}
\end{aligned}$$

$$4\tau_2 V_{ij} = (1 - S_{ij}S_{i+1})\{d_{ij} + a_{ij}^- S_{ij}\}, \tag{4}$$

$$4\tau_2 W_{ij} = (1 - S_{ij}S_{ij+1})\{e_{ij} + b_{ij}^- S_{ij}\}, \tag{5}$$

where the constant coefficients  $a_{ij}^\pm$ ,  $b_{ij}^\pm$ ,  $d_{ij}$ , and  $e_{ij}$  are related to the inhomogeneity matrix  $P_{ij}$ ,

$$\begin{aligned}
a_{ij}^\pm &= P_{i+1j} \pm P_{ij}, \\
b_{ij}^\pm &= P_{ij+1} \pm P_{ij}, \\
d_{ij} &= P_{ij} + P_{i+1j} - 2P_{ij}P_{i+1j}, \\
e_{ij} &= P_{ij} + P_{ij+1} - 2P_{ij}P_{ij+1}. \tag{6}
\end{aligned}$$

We proceed by deriving the rate equations for the one- and two-spin correlation functions, where the general  $n$ -spin function is given by

$$\langle S_{i_1 j_1}, \dots, S_{i_n j_n} \rangle = \sum_S S_{i_1 j_1}, \dots, S_{i_n j_n} P(S,t). \tag{7}$$

Using this and (2), some lengthy but straightforward calculations result in the following hierarchy of differential equations, using the renormalized time scale  $\tau$  defined by  $\tau^{-1} = \tau_1^{-1} + \tau_2^{-1}$ , and setting  $\tau_1 = \tau_2$ :

$$4\tau \frac{d}{dt} \langle S_{ij} \rangle = \Delta_{ij} \langle S_{ij} \rangle + (1 - 2P_{ij}) \langle S_{ij} \{ \Delta_{ij} S_{ij} \} \rangle, \tag{8}$$

$$\begin{aligned}
4\tau \frac{d}{dt} \langle S_{ij} S_{kl} \rangle = & (\Delta_{ij} + \Delta_{kl}) \langle S_{ij} S_{kl} \rangle + (1 - 2P_{ij}) \\
& \times \langle S_{ij} S_{kl} \{ \Delta_{ij} S_{ij} \} \rangle + (1 - 2P_{kl}) \\
& \times \langle S_{ij} S_{kl} \{ \Delta_{kl} S_{kl} \} \rangle \\
& \text{for } |i-k| + |j-l| > 1. \tag{9}
\end{aligned}$$

Here,  $\Delta_{ij} \langle S_{ij} \rangle = -4 \langle S_{ij} \rangle + \langle S_{i+1j} \rangle + \langle S_{i-1j} \rangle + \langle S_{ij+1} \rangle + \langle S_{ij-1} \rangle$  is the discrete Laplacian. For  $|i-k| + |j-l| = 1$ , i.e., for nearest-neighbor two-point correlations, the rate equation has a more complex form. For example,

$$\begin{aligned}
4\tau \frac{d}{dt} \langle S_{ij} S_{i+1j} \rangle = & (2d_{ij} - 8) \langle S_{ij} S_{i+1j} \rangle + \langle S_{i-1j} S_{i+1j} \rangle \\
& + \langle S_{ij} S_{i+2j} \rangle + \langle S_{ij} S_{i+1j+1} \rangle \\
& + \langle S_{ij} S_{i+1j-1} \rangle + \langle S_{ij-1} S_{i+1j} \rangle \\
& + \langle S_{ij+1} S_{i+1j} \rangle + (1 - 2P_{ij}) \\
& \times \{ \langle S_{i-1j} S_{ij} S_{i+1j} \rangle - \frac{3}{2} \langle S_{i+1j} \rangle \} \\
& + (1 - 2P_{i+1j}) \{ \langle S_{ij} S_{i+1j} S_{i+2j} \rangle \\
& - \frac{3}{2} \langle S_{ij} \rangle \} + 2(1 - d_{ij}). \tag{10}
\end{aligned}$$

In the homogeneous limit  $P_{ij} \rightarrow \frac{1}{2}$ , the results in [6] are recovered.

### III. TWO-SITE DISORDER

We now turn to the case where  $P_{ij}$  can take just two different values,  $p$  or  $q = 1 - p$ , with an equal number of  $p$  sites and  $q$  sites. This corresponds to the model given in [9] with equal fluxes of  $A$  and  $B$  species,  $\epsilon = |p - \frac{1}{2}|$  and  $c_- = c_+ = \frac{1}{2}$ , using the notation given there.

Since  $p + q = 1$ , the global dynamics of the system must be unchanged under the transformation  $(p, q) \rightarrow (1 - p, 1 - q) = (q, p)$ . This symmetry means that the system cannot favor one state over the other, and so the average of  $\langle S_{ij} \rangle$  taken over the entire  $L \times L$  lattice,  $(1/L^2) \sum_{i,j} \langle S_{ij} \rangle$ , will always tend to zero in the  $L \rightarrow \infty$  limit. An important consequence of this is that if a finite system always saturates, then it does so with equal probability of saturating either to every site being  $+1$ , or every site being  $-1$ , and so  $\langle S_{ij} \rangle|_{t=\infty} = 0 \forall i, j$ , regardless of whatever  $P_{ij}$  may be. If a reactive steady state occurs—that is, if the average saturation time diverges at least as fast as  $e^{L^2}$  [5]—then it should be expected that  $\langle S_{ij} \rangle$  may be nonzero for  $t \rightarrow \infty$  (if  $p \neq \frac{1}{2}$ ). It is the purpose of this section to apply the rate equations derived in Sec. II to predict the equilibrium value of  $\langle S_{ij} \rangle$  on  $p$  sites in any such nontrivial steady state.

Although the concentrations of  $p$  sites and  $q$  sites are equal, different arrangements of the sites can dramatically alter the long-time dynamics of the system. For instance, choosing to split the lattice into two alternating  $c(2 \times 2)$  sublattices, with one sublattice full of  $p$  sites and the other full of  $q$  sites, results in a system with no nontrivial steady states for  $p \neq 0$  or  $1$ . Since saturation always occurs,  $\langle S_{ij} \rangle|_{t=\infty} = 0$  on either type of site.

A more informative model can be constructed by ran-

domly arranging the  $p$  and  $q$  sites. This allows for regions of  $p$  sites, which will all tend to be fixed into the same state, and regions of  $q$  sites, which will all tend to be fixed into the other state, to “pin” the dynamics into a reactive equilibrium.

When  $p=q=\frac{1}{2}$ , we simply have the original homogeneous model with its associated kinetic phase—the distinction between the two sorts of site is lost. For  $p=0$  or 1, the kinetics become entirely trivial, the only randomness coming from the choice of which sites are to be checked for reaction, and after  $O(L^2)$  reactions the system reaches a steady state in which boundaries between regions of  $p$  and  $q$  sites are constantly reacting, but never moving.

More interesting, however, are the dynamics for  $p \neq 0, \frac{1}{2},$  or 1, when the system approaches a reactive steady state exponentially in time. A useful mean-field theory can be constructed by assuming that every site is surrounded by exactly two  $p$  sites and two  $q$  sites. It is then possible to write down (8) and (10) for the two sorts of site,  $\langle S_{ij} \rangle_p$  and  $\langle S_{ij} \rangle_q$ , and the various two-point functions. To obtain a closed set of equations, however, further approximations must be made to reduce the three-point functions in (10) to one- and two-point functions. The obvious choice is

$$\langle S_{ij}S_{kl}S_{mn} \rangle \approx \langle S_{ij}S_{kl} \rangle \langle S_{kl}S_{mn} \rangle, \quad (11)$$

but this is no longer asymmetric under  $S_{kl} \rightarrow -S_{kl}$ , which would result in  $\langle S_{ij} \rangle_p + \langle S_{ij} \rangle_q \neq 0$ , something which cannot be true since  $p+q=1$ . To restore the required symmetry we must also include, where appropriate, the alternative three-point approximation,

$$\langle S_{ij}S_{kl}S_{mn} \rangle \approx \langle S_{ij} \rangle \langle S_{kl}S_{mn} \rangle. \quad (12)$$

For greater clarity, we denote the one-spin correlation function  $\langle S_{ij} \rangle_p = -\langle S_{ij} \rangle_q$  by  $y_p$ , the two-spin correlation function between two NN  $p$  sites (or, equivalently, two NN  $q$  sites) by  $z_{pp}$ , and use  $z_{pq}$  for the two-point function between nearest-neighbor  $p$  and  $q$  sites. Setting  $\tau=1$ , we can now obtain a closed set of equations,

$$2 \frac{d}{dt} y_p = -2y_p + (1-2p)(z_{pq} + z_{pp} - 2), \quad (13)$$

$$4 \frac{d}{dt} z_{pp} = (4pq - 8)z_{pp} - 3(1-2p)y_p + \{(1-2p)y_p + 3z_{pp}\} \times (z_{pp} + z_{pq}) + (2-4pq), \quad (14)$$

$$4 \frac{d}{dt} z_{pq} = 4pq - (4pq + 6)z_{pq} + 3(1-2p)y_p + 3z_{pq}(z_{pp} + z_{pq}). \quad (15)$$

The most constructive way to test the validity of this analysis is to compare the value of  $y_p$  at equilibrium, as predicted by (13)–(15), to numerical simulations. We iterated the equations using a computer algebra package, with the initial conditions  $y_p|_{t=0} = z_{pp}|_{t=0} = z_{pq}|_{t=0} = 0$ , until a steady state became evident. For the simulation runs, we used the corresponding initial conditions of a lattice randomly filled with +1's or -1's. Again, the simulations were

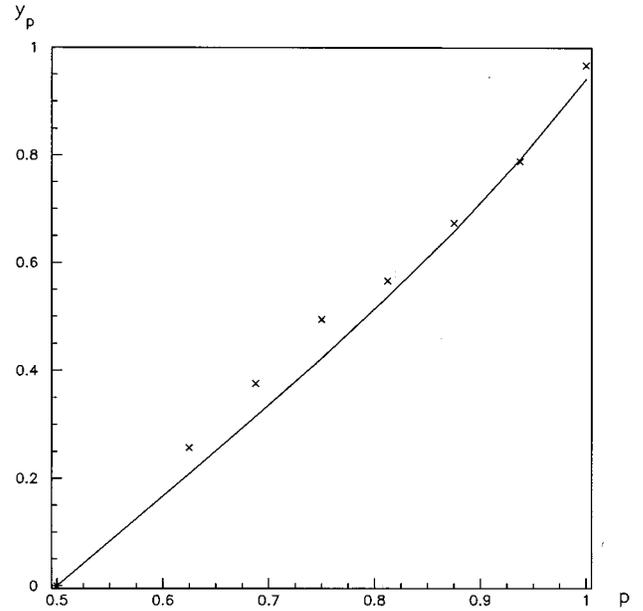


FIG. 1. Plot of  $p$  vs  $y_p|_{t=\infty}$ . The line gives the values predicted by the rate equations. Numerical simulation results are plotted as crosses. The simulations were performed on a  $200 \times 200$  lattice, and averaged over 100 runs.

continued until an equilibrium state was apparent. The two different sets of values for  $y_p|_{t=\infty}$  are compared in Fig. 1, where the simulation results compare favorably with the approximate analysis, the agreement improving for larger values of  $p$ . Note that even when  $p=0$  or 1,  $y_p$  still does not tend to  $\pm 1$ , either in theory or in the numerical work. This is because the system will now include configurations of jammed sites. For instance, in the case of  $p=1$ , a  $q$  site surrounded by four  $p$  sites may initially start at +1 but be unable to change, since if all four NN  $p$  sites get fixed into a +1 state before they have reacted with the central  $q$  site, then the  $q$  site will never be able to react and so it will stay at +1 for all time, despite the fact that it has  $P_{ij}=0$ .

The discrepancy for  $p \approx \frac{1}{2}$  can be explained by considering when the approximations employed are valid. The reduction of three-point functions to one- and two-point functions given in (11) and (12) will fail when there exist large domains of sites in the same state. To see why this is the case, consider a group of three adjacent sites. Each site is in either a +1 state or a -1 state, so we can, for instance, use (+++) to denote the case when all three sites are in the +1 state, and so on, for the other seven possible combinations. Now, when  $p=0$  or 1, the state of each site will be fixed by whether it is a  $p$  site or a  $q$  site, and, if we ignore jamming effects, the site will be independent of its neighbors. Thus, taken over the entire lattice, each of the eight possible configurations, (+++), (++-), (+-+), ..., (---), have equal weightings. A brief analysis shows that the approximations are now in fact exact. However, within domains of similar states, there will only be two equiprobable configurations, (+++) and (---), and the approximations now fail. Since domain coarsening is associated with  $p \approx \frac{1}{2}$ , we should expect the mean-field theory to break down here. Note that, as can be seen from Fig. 1, the theory does manage to predict the exact answer for  $p = \frac{1}{2}$ . This is due to noth-

ing more than (13) decoupling from the other rate equations, giving rise to the trivial solution  $y_p(t) \equiv 0$ .

The analysis in this section can be easily extended to other inhomogeneity matrices. For instance, it is possible to construct a mean-field theory for the case of the alternating  $c(2 \times 2)$  sublattices. For small times the theory agrees well with experiment, but once saturation effects start to occur the approximations again break down and fail to predict the correct answer of  $y_p \rightarrow 0$ .

#### IV. INHOMOGENEOUS DESORPTION

We now turn to an enhanced model studied by Fichthorn, Gulari, and Ziff [11], which introduces noise into the system in the form of the desorption of  $A$  and  $B$  species from the substrate. They demonstrated numerically, later confirmed by mean-field analysis [12], that even a small desorption rate induces steady-state reactivity onto finite lattices. In our version of the model, sites vacated by desorption are refilled by an  $A$  or a  $B$  as defined by the inhomogeneity matrix, which we now call  $Q_{ij}$ .  $Q_{ij}$  differs from  $P_{ij}$  in that now it *only* applies to sites refilled after desorption—sites vacated after an  $A+B \rightarrow 2S$  reaction have an equal chance of being refilled either by an  $A$  or by a  $B$ . Thus, the reaction kinetics alone are the same as the usual homogeneous model, and the  $U_{ij}$ ,  $V_{ij}$ , and  $W_{ij}$  operators without the desorption take their simpler form found by setting  $P_{ij} = \frac{1}{2}$  in (3)–(5). Explicitly,

$$8\tau_1 U_{ij}(S) = 4 - S_{ij}(S_{i+1j} + S_{i-1j} + S_{ij+1} + S_{ij-1}), \quad (16)$$

$$8\tau_2 V_{ij}(S) = 1 - S_{ij}S_{i+1j}, \quad (17)$$

$$8\tau_2 W_{ij}(S) = 1 - S_{ij}S_{ij+1}. \quad (18)$$

To include inhomogeneous desorption within this formulation, we replace  $U_{ij}$  with  $U_{ij}^d$ ,

$$U_{ij}^d = U_{ij} + \frac{1}{2\tau_3} \{1 + S_{ij}(1 - 2Q_{ij})\}, \quad (19)$$

where, as in [6], we introduce a renormalized time scale  $\tau$  and the spin-flip parameter  $\gamma$ , defined by

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \frac{1}{\tau_3}, \quad (20)$$

$$\gamma = 1 - \tau/\tau_3. \quad (21)$$

The one-point spin-correlation rate equation can now be recalculated using (2) and (16)–(19),

$$4\tau \frac{d}{dt} \langle S_{ij} \rangle = \gamma \Delta_{ij} \langle S_{ij} \rangle - 4(1 - \gamma) \{ \langle S_{ij} \rangle + (1 - 2Q_{ij}) \}. \quad (22)$$

This can be solved by using a generating function,  $G(X, Y, t)$ , defined in terms of the time-dependent one-spin correlation function  $\langle S_{ij} \rangle$ ,

$$G(X, Y, t) = \sum_{i=-\infty}^{\infty} \sum_{j=-\infty}^{\infty} X^i Y^j \langle S_{ij} \rangle. \quad (23)$$

Combining this with (22) gives rise to a differential equation for  $G$ ,

$$\begin{aligned} \frac{\partial G}{\partial t} = \frac{G}{\tau} \left\{ \frac{\gamma}{4} \left( X + \frac{1}{X} + Y + \frac{1}{Y} \right) - 1 \right\} \\ - \frac{1}{\tau_3} \sum_{i,j=-\infty}^{\infty} X^i Y^j (1 - 2Q_{ij}). \end{aligned} \quad (24)$$

Noting that, except for  $G(X, Y, t)$ , the right-hand side of (24) is independent of time, it is not difficult to derive an explicitly time-dependent expression for  $\langle S_{ij} \rangle$  in terms of its initial state,  $\sigma_{ij} = \langle S_{ij} \rangle|_{t=0}$ ,

$$\begin{aligned} \langle S_{ij} \rangle = e^{-t/\tau} \sum_{k,l=-\infty}^{\infty} \sigma_{kl} I_{i-k} \left( \frac{\gamma t}{2\tau} \right) I_{j-l} \left( \frac{\gamma t}{2\tau} \right) \\ - \frac{1}{\tau_3} \sum_{k,l=-\infty}^{\infty} (1 - 2Q_{kl}) \int_0^t e^{-t'/\tau} I_{i-k} \left( \frac{\gamma t'}{2\tau} \right) \\ \times I_{j-l} \left( \frac{\gamma t'}{2\tau} \right) dt', \end{aligned} \quad (25)$$

where  $I_i(t)$  is the  $i$ th-order modified Bessel function. In the special case  $\Delta_{ij} Q_{ij} = 0$ , it is possible to rewrite the second term on the right-hand side of (25) as

$$\begin{aligned} - \frac{1}{4\tau_3} \sum_{k,l=-\infty}^{\infty} (1 - 2Q_{kl}) \{ f_{i-k+1j-l} + f_{i-k-1j-l} \\ + f_{i-kj-l+1} + f_{i-kj-l-1} \}, \end{aligned} \quad (26)$$

where for clarity we have introduced

$$f_{ij}(t) = \int_0^t e^{-t'/\tau} I_i \left( \frac{\gamma t'}{2\tau} \right) I_j \left( \frac{\gamma t'}{2\tau} \right) dt', \quad (27)$$

which obeys the identity

$$\begin{aligned} f_{i+1j} + f_{i-1j} + f_{ij+1} + f_{ij-1} \\ = \frac{4}{\gamma} f_{ij} - \frac{4\tau}{\gamma} \delta_{i0} \delta_{j0} + \frac{4\tau}{\gamma} e^{-t/\tau} I_i \left( \frac{\gamma t}{2\tau} \right) I_j \left( \frac{\gamma t}{2\tau} \right), \end{aligned} \quad (28)$$

with  $\delta_{ij}$  the usual Kröneckner delta. Substituting (28) into (25) and (26) results in an exact expression,

$$\begin{aligned} \langle S_{ij} \rangle = 2Q_{ij} - 1 + e^{-t/\tau} \sum_{k,l=-\infty}^{\infty} (1 - 2Q_{kl} + \sigma_{kl}) \\ \times I_{i-k} \left( \frac{\gamma t}{2\tau} \right) I_{j-l} \left( \frac{\gamma t}{2\tau} \right). \end{aligned} \quad (29)$$

So when  $\Delta_{ij} Q_{ij} = 0$ ,  $\langle S_{ij} \rangle \rightarrow 2Q_{ij} - 1$  exponentially as  $t \rightarrow \infty$ , again in agreement with the homogeneous result of [11]. With desorption, jamming is no longer possible and so now  $\langle S_{ij} \rangle \rightarrow 1$  when  $Q_{ij} = 1$ . Although this final solution is exact, it is hard to see what physical applications a mixed homogeneous and/or inhomogeneous model such as this one may have.

### V. INHOMOGENEOUS ONE-SPECIES DESORPTION

While investigating the monomer-dimer model, Ziff, Gulari, and Barshad [1] briefly discussed the additional feature of allowing just the monomers to desorb. Physically, this corresponds to the reaction  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$  where only the CO can desorb from the substrate, which is a good approximation for this reaction at the usual operating temperatures.

To apply a similar principle to our monomer-monomer model, we extend the analysis in Sec. IV to allow for the desorption of  $A$  species only, with the inhomogeneity matrix  $Q_{ij}$  only applying to sites vacated after desorption. Thus, the flip-exchange operators are unchanged from (16)–(18), but now we replace  $U_{ij}$  with

$$U_{ij}^d = U_{ij} + \frac{1 - Q_{ij}}{2\tau_3} (1 + S_{ij}). \quad (30)$$

Furthermore,  $Q_{ij}$  is also taken to be a constant matrix,  $Q_{ij} = q \forall i, j$ . The rate equation for the one-spin correlation function (22) is now

$$4\tau \frac{d}{dt} \langle S_{ij} \rangle = \Delta_{ij} \langle S_{ij} \rangle - \gamma(1 - q)(1 + \langle S_{ij} \rangle). \quad (31)$$

The definitions of  $\tau$  and  $\gamma$  have now altered from the previous case,

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2}, \quad (32)$$

$$\gamma = \frac{4\tau}{\tau_3}. \quad (33)$$

Applying the same generating function (23) results in a new partial differential equation for  $G(X, Y, t)$  acting on an  $L \times L$  lattice,

$$\frac{\partial G}{\partial t} = \frac{G}{\tau} \left\{ \frac{1}{4} \left( X + \frac{1}{X} + Y + \frac{1}{Y} \right) - 1 \right\} - \frac{1 - q}{\tau_3} (G + L^2). \quad (34)$$

Continuing as before, an explicit time-dependent expression for  $\langle S_{ij} \rangle$  is reached,

$$\begin{aligned} \langle S_{ij} \rangle = & e^{-t[1/\tau + (1-q)/\tau_3]} \sum_{k,l=-L/2}^{L/2} \sigma_{kl} I_{i-k} \left( \frac{t}{2\tau} \right) I_{j-l} \left( \frac{t}{2\tau} \right) \\ & - \frac{(1-q)L^2}{\tau_3} \int_0^t \exp \left[ -t' \left( \frac{1}{\tau} + \frac{1-q}{\tau_3} \right) \right] \\ & \times I_i \left( \frac{t'}{2\tau} \right) I_j \left( \frac{t'}{2\tau} \right) dt'. \end{aligned} \quad (35)$$

### VI. CONCLUSIONS AND DISCUSSION

We have introduced a methodology for dealing with the effects of generalized surface disorder on the monomer-monomer reaction process  $A + B \rightarrow 2S$  by mapping the system in the reaction-controlled limit onto an Ising model. The two-dimensional rate equations were derived, including the very concise one-spin correlation equation (8), and used to study the special case of two-site disorder. Here, it was found that the global system dynamics are sensitive to the choice of layout of the two different types of site. Catalysts consisting of two different molecules arranged in a regular manner, such as on two alternating  $c(2 \times 2)$  sublattices, allow for no reactive equilibrium and will always saturate on finite lattices. Choosing to randomly arrange the sites, however, allowing compact clusters of the same site, was shown to produce a reactive steady state. Analysis based on the rate equations was used to predict the concentration of  $A$ 's and  $B$ 's on the different types of site, showing reasonable agreement between theory and simulation despite the rather crude approximations involved in the analysis. The model was then extended to include desorption from the substrate, either by one or both species, and was solved exactly in both cases.

Extending this work to dimensions other than  $d=2$  is straightforward once the mapping onto the Ising model has been achieved. Indeed, the rate equations for  $d=1$  can be immediately seen from those given here (8)–(10). We have focused on  $d=2$  since the most useful physical application is of surface catalysis.

It should be noted that the definition of inhomogeneity we chose to employ here is only one of many ways of modeling surface disorder. For instance, requiring that each site be ‘hit’ a different number of times before adsorbing a particle, or assigning a quenched random ‘energy’ to each site and always adsorbing the particles onto the vacant site with the lowest energy, are just two alternative possibilities. We intend to study some of these in future work.

[1] R. Ziff, E. Gulari, and Y. Barshad, Phys. Rev. Lett. **56**, 2553 (1986).  
 [2] R. Ziff and K. Fichthorn, Phys. Rev. B **34**, 2038 (1986).  
 [3] P. Meakin and D. Scalapino, J. Chem. Phys. **87**, 731 (1987).  
 [4] J. Evans and T. Ray, Phys. Rev. E **47**, 1018 (1993).  
 [5] D. ben-Avraham, S. Redner, D. B. Considine, and P. Meakin, J. Phys. A **23**, L613 (1990).  
 [6] P. L. Krapivsky, Phys. Rev. A **45**, 1067 (1992).  
 [7] J. Zhuo, S. Redner, and H. Park, J. Phys. A **26**, 4197 (1993).

[8] D. Vlachos, L. Schmidt, and R. Aris, J. Chem. Phys. **93**, 8306 (1990).  
 [9] L. Frachebourg, P. L. Krapivsky, and S. Redner, Phys. Rev. Lett. **75**, 2891 (1995).  
 [10] G. Forgacs, D. Mukamel, and R. A. Pelcovits, Phys. Rev. B **30**, 205 (1984).  
 [11] K. Fichthorn, E. Gulari, and R. Ziff, Phys. Rev. Lett. **63**, 1527 (1989).  
 [12] D. Considine, S. Redner, and H. Takayasu, Phys. Rev. Lett. **63**, 2857 (1989).