

# Kinetics of Catalysis with Surface Disorder

D.A.Head and G.J.Rodgers

Department of Physics, Brunel University, Uxbridge,  
Middlesex. UB8 3PH, UK

## Abstract

We study the effects of generalised 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.

PACS numbers: 05.70.Ln, 82.65.Jv, 82.20.Mj

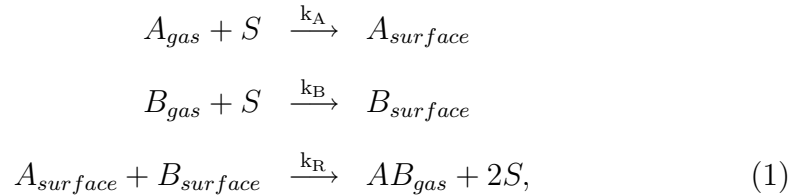
e-mail: David.Head@brunel.ac.uk, G.J.Rodgers@brunel.ac.uk

October 31, 2006



## 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  $2CO + O_2 \rightarrow 2CO_2$  on a catalytic surface. A well-studied variant [2, 3, 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 modelling actual chemical processes, including nearest neighbour excluded adsorption [7] and surface diffusion [4, 8]. However, only re-



cently 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 which favours adsorption by the A-species, and one which favours 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 organised as follows. In section II we define the model and derive the general rate equations for the n-spin correlation functions. In section III, these equations are applied to a model similar to that in [9] and their solutions are compared to numerical simulations. In sections 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 summarised in section 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-neighbour (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 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

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

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

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

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

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

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

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

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



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

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

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

$$\begin{aligned} 4\tau \frac{d}{dt} \langle S_{ij} S_{kl} \rangle &= (\Delta_{ij} + \Delta_{kl}) \langle S_{ij} S_{kl} \rangle \\ &+ (1 - 2P_{ij}) \langle S_{ij} S_{kl} \{ \Delta_{ij} S_{ij} \} \rangle \\ &+ (1 - 2P_{kl}) \langle S_{ij} S_{kl} \{ \Delta_{kl} S_{kl} \} \rangle. \end{aligned} \quad (9)$$

... for  $|i - k| + |j - l| > 1$

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 neighbour 2-point correlations, the rate equation has a more complex form. For example,



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

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 favour one state over the other, and so the average of  $\langle S_{ij} \rangle$  taken over the entire  $L \times L$  lattice,  $\frac{1}{L^2} \sum_{i,j} \langle S_{ij} \rangle$ , 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 non-zero for  $t \rightarrow \infty$  (if  $p \neq \frac{1}{2}$ ). It is the purpose of this section to apply the rate equations derived in section II to predict the equilibrium value of  $\langle S_{ij} \rangle$  on  $p$ -sites in any such non-trivial 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 non-trivial 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 randomly 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. Although exact analysis of this model is obviously impossible, a useful approximation can be made by assuming that every site is surrounded by exactly 2  $p$ -sites and 2  $q$ -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, 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 has the unwanted side-effect that  $\langle S_{ij} \rangle_p + \langle S_{ij} \rangle_q \neq 0$ , something which cannot be true since  $p + q = 1$ . To restore the required symmetry we must also include an 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 neighbour  $p$  and  $q$  sites. Setting  $\tau = 1$ , we can now obtain a closed set of equations,

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

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

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

The most constructive way to test the validity of this analysis is to compare the value of  $y_p$  at equilibrium, as predicted by iterating eqns.(13–15),



to numerical simulations. In these simulations, the sites are initially randomly filled with +1's or -1's, so the corresponding initial conditions for the iteration procedure are  $y_p|_{t=0} = z_{pp}|_{t=0} = z_{pq}|_{t=0} = 0$ . The results are compared in fig.1., where the simulation results compare favourably with the approximate analysis, the agreement improving for larger values of  $p$ .

Note that even when  $p = 1$ ,  $y_p$  does *not* tend to +1, either in the theory or in the numerical work. This is because it is possible to have a jammed state where, for instance, a  $q$ -site surrounded by 4  $p$ -sites may initially start at +1 but be unable to change, since if all 4 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 as +1 for all time, despite the fact that it has  $P_{ij} = 0$ .

#### 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 renormalised 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-dependant 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  $G$ ,

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

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,  $\sigma_{ij} = \langle S_{ij} \rangle|_{t=0}$ ,

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

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



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

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

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

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

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

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 homo/inhomogeneous model such as this one may have.



## V. INHOMOGENEOUS ONE-SPECIES DESORPTION

Whilst 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  $2CO + O_2 \rightarrow 2CO_2$  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 section 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,

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

## VI. CONCLUSIONS AND DISCUSSION

We have introduced a methodology for dealing with the effects of generalised 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 modelling 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.





## References

- [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).



Figure 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.



