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## LETTER TO THE EDITOR

### Exact dynamics of a bistable chemical reaction model

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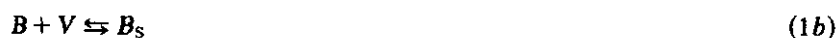
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**Abstract.** Dynamics of the chemical reaction model introduced by Fichthorn *et al* is discussed along the lines of our previous work. We find that the steady-state reaction rate is reached as  $1/\sqrt{t}$  in Euclidean dimension  $d = 1$  and  $d = 2$  is the marginal dimension. The distinction made between the segregation regime and the saturation regime is recovered for the transient regime.

There has been a good deal of interest recently in the study of kinetic models for surface reactions. These models are an important class of problems in statistical physics in which dynamical behaviour clearly departs from that expected in a mean-field theory. Also the study of these oversimplified models may help to elucidate the complex behaviour of actual catalytic reactions on surfaces. For review articles in the field, see [1, 2]. A case in point is the model of Fichthorn, Gulari and Ziff (FGZ) [3] for heterogeneous catalytic surface reactions. It belongs to a class of monomer-monomer reactions on a saturated surface and exhibits a bistability transition [3-5]. In a recent publication Clément *et al* [6] have solved the problem exactly in the steady state, and they have shown that the transition is controlled by the desorption probability, the Euclidean dimension and the finite size of the substrate. Furthermore, it has been shown that a self-organization of reactants called segregation is present in dimensions lower than two. In this letter, we propose to pursue the study and we solve exactly the problem of the approach to the steady state. We show that a slowing down of the reaction occurs as a consequence of the growth of domains and that a dynamical transition to a poisoned state may occur before a reactive steady state is reached.

The FGZ model is of the Langmuir-Hinshelwood type



Here  $A$  and  $B$  are gas phase reactants which are adsorbed on the vacant sites  $V$  of the surface. When two unlike adsorbed species are nearest neighbours they interact and both vacant sites are filled by  $A$  or  $B$  with equal probability. The control parameter

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of the dynamical system is the probability  $p$  that an adsorbed species desorbs to be replaced by either  $A$  or  $B$  with equal probability. This model has been studied by Monte Carlo simulations [3, 4]: it has been found that at low  $p$  the system stays in a nearly non-reactive state associated with a nearly complete coverage by a single species (*poisoning*). However, for finite  $p$  there exists a finite probability for a  $B_S$  ( $A_S$ ) island to grow on an  $A_S$  ( $B_S$ ) covered surface and the system may flip towards the other poisoned state (*bistability*). A mean-field treatment of this model [5] reproduces the bistability transition. We have shown [6] that this reaction-limited kinetic model is amenable to an *exact* treatment through a master equation of the probability  $P(\{z\})$  of a given configuration  $\{z\}$ . We define a state variable  $z_i$  such that  $z_i = 1$  if the site is occupied by  $A$ ,  $z_i = -1$  if occupied by  $B$ . The equal-time correlation function  $m_r = (1/N) \sum_i \langle z_i z_{i+r} \rangle$  obeys

$$\dot{m}_{r(t)} = 2D\Delta m_{r(t)} - 2pm_r(t) - 2DQ(t) \sum_{\alpha} \delta_{\alpha,r} + 2(2Q(t) + p)\delta_{0,r}. \quad (2)$$

This equation is an exact consequence of the master equation [6]. In (2)  $D = 1/2d$  is an effective diffusion constant where  $d$  is the space dimension,  $\alpha$  denotes the nearest neighbours and the reaction probability  $Q(t)$  is related to the nearest-neighbour correlation function,  $2Q(t) = 1 - m_{\alpha}(t)$ . One finds for the steady state†:

$$Q_{ss} = \frac{1}{2} \frac{1 - pF(L, p)}{1 + (1 - p)F(L, p)/2} \quad (3)$$

where

$$F(L, p) = \frac{1}{N} \sum_q \frac{\cos(2\pi q_{\alpha}/L)}{p + \sum_j [1 - \cos(2\pi q_j/L)]}. \quad (4)$$

In (4),  $N = L^d$  is the number of atoms on the lattice of size  $L$ . The saturation parameter  $\Delta_{ss} = (N_A - N_B)^2/N^2$ , turns out to be

$$N\Delta_{ss} \equiv Nm_{q=0} = 1 + Q_{ss}/p. \quad (5)$$

This treatment is valid for all dimensions. For  $d \geq 3$ , mean-field behaviour [5] is recovered. For  $d \leq 2$  a non-trivial fluctuation-controlled behaviour is found. Depending on the value of  $p$ , two regimes may be singled out for  $F$  and thus for  $Q_{ss}$  and  $\Delta_{ss}$ .

(i) For  $p < p_c$  where  $p_c$  is a cross-over value, the sum in (4) is dominated by its first term and  $F = 1/Np$ .

(ii) For  $1 > p > p_c$  one can replace the sum by an integral:

$$d = 1: \quad F \sim \frac{1}{\sqrt{2p}} \quad \text{and} \quad p_c \approx \frac{1}{N^2} \quad (6a)$$

$$d = 2: \quad F \sim 0.056 - \frac{1}{2\pi} \ln p \quad \text{and} \quad p_c \ln\left(\frac{1}{p_c}\right) \approx \frac{1}{N}. \quad (6b)$$

In the first regime the system is *saturated* (i.e.  $\Delta_{ss} \approx 1$ ), while in the second there is a *segregation* over domains of size  $1 < \Lambda < L$ .

† In this non-equilibrium model the adsorption step is reversible whereas the reaction step is not. The finite desorption probability amounts to a mixing which allows a steady state to form. In this respect the model differs from the monomer-monomer model in which the reaction step is reversible and the adsorption step is not, this model has been studied by ben-Avraham *et al* [7].

We will now show that the transition from segregated ( $p > p_c$ ) to saturated ( $p < p_c$ ) affects the way the system relaxes to steady state. We give analytic arguments supported by simulations. We start with the equation of motion for the correlation function (2). Taking the Laplace transform  $\tilde{m}_q(s)$  of  $m_q(t)$  one gets

$$2\tilde{m}_q(s) \left[ p + \frac{s}{2} + \frac{1}{d} \sum_j \left( 1 - \cos \frac{2\pi q_j}{L} \right) \right] = m_q(t=0) + \frac{2p}{Ns} + \frac{2\tilde{Q}(s)}{N} \left[ 1 + \frac{1}{d} \sum_j \left( 1 - \cos \frac{2\pi q_j}{L} \right) \right] \quad (7)$$

where the initial conditions enter in  $m_q(t=0)$ . This leads to

$$\tilde{Q}(s) = \frac{1}{s} \frac{1 - pF(L, p^*)}{2 + (1 - p^*)F(L, p^*)} - \frac{1}{2[2 + (1 - p^*)F(L, p^*)]} \times \sum_q \frac{m_q(t=0) \cos(2\pi q_1/L)}{p^* + (1/d) \sum_j [1 - \cos(2\pi q_j/L)]} \quad (8)$$

where  $p^* = p + s/2$ . For a random initial condition  $m_q(t=0) = 1/N$ . A central role is played by the function  $\Phi = F(L, p^*)$ . From now on we deal with the transient regime, i.e. with time much lower than  $p^{-1}$ . In this case,  $p^* \approx s/2$  and  $\phi \approx F(s/2)$  and we see by analogy with the results of [4] that we have two limiting regimes as well. For intermediate values of the desorption parameter, i.e.  $p > p_c$  ( $p_c$  is the cross-over value of equations (6)), we obtain the segregation regime and:

$$\text{in } d = 1: \quad \tilde{Q}(s) \approx \frac{1}{\sqrt{s}} \quad \text{thus } Q(t) \approx \frac{1}{\sqrt{t}} \quad \text{and} \quad \Delta(t) \approx \frac{4}{N} \sqrt{\frac{t}{\pi}} \quad (9a)$$

$$\text{in } d = 2: \quad \tilde{Q}(s) \approx \frac{1}{s[2.16 - (1/2\pi) \ln s]} \quad (9b)$$

$d = 2$ , is the marginal dimension and the limiting regime  $(s \ln s)^{-1}$  is, in practice, hardly accessible. Note that we rather tested on simulation an intermediate regime where the logarithmic term is smaller than 2.16. In this case the time dependence is:

$$Q(t) \approx 0.377 - 0.021 \ln t.$$

The slowing down of the dynamics is mainly due to the occurrence of a segregation scale. The second regime is observed for smaller desorption parameters, i.e. for  $p < p_c$ . In this case the early time is a segregated regime since  $s > p_c$  but for longer time ( $t > p_c^{-1}$ ) we have a sharp transition to a poisoned regime since the leading value of  $\Phi \approx 2/Ns$ , therefore:

$$Q(s) \approx N/2 \quad \text{thus } Q(t) \approx 0 \quad \text{and} \quad \Delta(t) \approx 1.$$

This poisoned regime will last until the population is renewed, i.e. for time scales of the order of  $p^{-1}$ .

Behaviour of the sort we have found is illustrated in figures 1(a) and 1(b) on which we have plotted  $Q$  versus time (in Monte Carlo steps) and  $\Delta$  versus time for values of  $p$  above and below  $p_c$  together with the theoretical results for  $d = 1$ . These simulations have been performed for an  $L = 256$  lattice, thus  $p_c = 3 \times 10^{-5}$  and  $t_c = 1.6 \times 10^4$ . Figure 2 illustrates the same behaviour for  $d = 2$  for the reaction rate  $Q(t)$ . We have taken a  $64 \times 64$  lattice† for which  $p_c = 8.2 \times 10^{-5}$  and  $t_c = 6.1 \times 10^3$ .

† Note that at  $p_c < p < 1$  the integral approximates the sum in (4) only for large  $L$ .

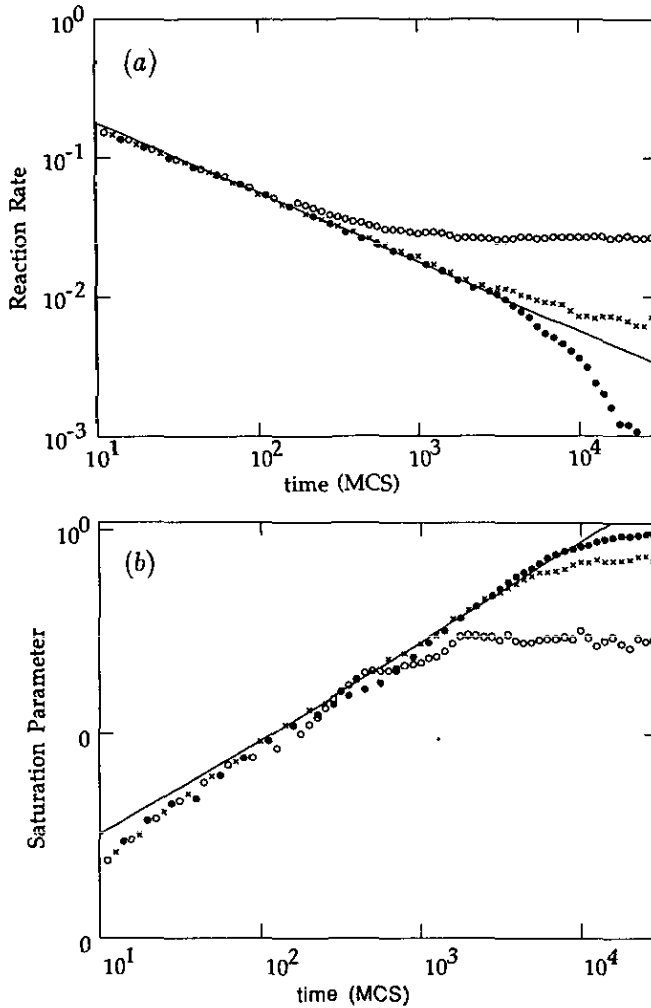


Figure 1. Time evolution of (a) the reaction rate  $Q(t)$  and (b) the saturation parameter  $\Delta(t)$ , for  $d=1$  and  $L=256$ . (○):  $p=0.39 \times 10^{-2}$ , (×):  $p=0.39 \times 10^{-3}$  and (●):  $p=0.39 \times 10^{-5}$ . Solid line:  $Q(t) = (1/\sqrt{\pi t})\Delta(t) = (1+4\sqrt{t/\pi})/L$ .

A central result of our previous investigations [6] was a simple universal scaling with the number of sites  $N = L^d$ . At steady state  $NQ^{ss}$  and  $\Delta^{ss}$  depend only on a reduced variable  $X$ :  $X = Np^{1/2}$  ( $d=1$ ),  $X = Np \ln(1/p)$  ( $d=2$ ). This result arises from the simple dependence of  $Q^{ss}$  as a function of  $F$ . Here, we also expect universal behaviour of  $NQ(t)$  and  $\Delta(t)$ . This is shown in figure 3 on which we have plotted the results of simulations for  $d=1$  and for various lattice sizes  $L$  and corresponding values of  $p$  below and above  $p_c$ , as  $QL$  versus  $t/L^2$  curves for different sizes collapse on a master curve.

Calculations proceed along the same lines for other initial conditions. For example, for an initially saturated system with  $p > p_c$  we have  $m_q(t=0) = \delta_{q,0}$ . Thus for  $d=1$  the leading term is  $\hat{Q}(s) \approx 2p/s\sqrt{s}$  and thus  $Q(t) \approx 4p\sqrt{t/\pi}$ . Note that now  $Q(t)$  depends on  $p$ . In figure 4 we compare the results of simulations for two values of  $p$  with the predicted limiting behaviour.

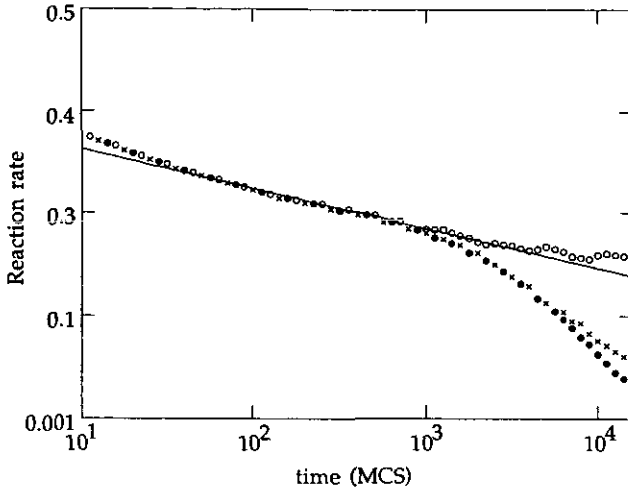


Figure 2. Reaction rate as a function of time for  $d=2$  and  $L=64$ . (O):  $p=0.18 \times 10^{-3}$ , (x):  $p=0.18 \times 10^{-4}$ , (●):  $p=0.18 \times 10^{-5}$ . Solid line:  $Q(t) = 0.377 - 0.021 \ln t$ .

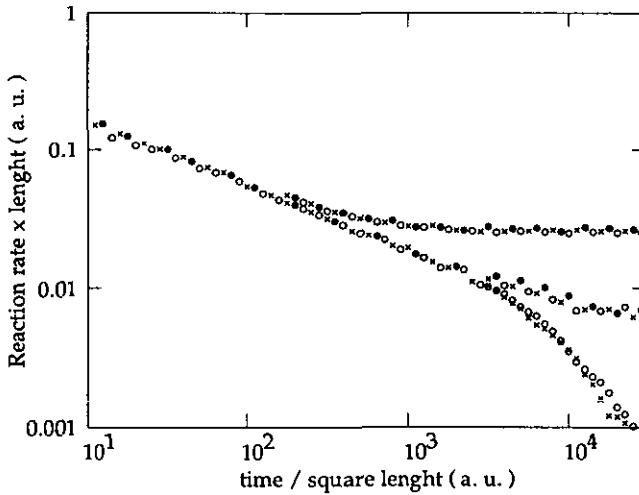
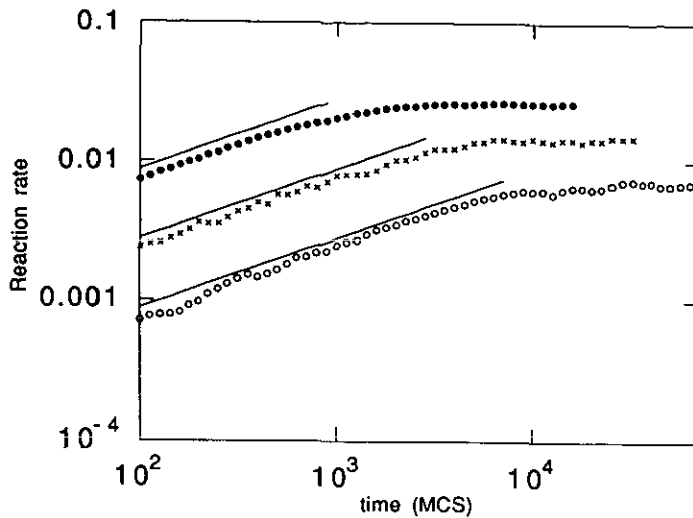


Figure 3. Reaction rate as a function of time plotted as  $Q(t)L$  versus  $t/L^2$  in  $d=1$  for  $X=16$  (upper curve),  $X=5$  (intermediate curve) and  $X=1.6$  (lower curve). (O)  $L=218$ , (x):  $L=256$ , (●):  $L=512$ .

In conclusion, we have seen how spontaneous spatial organization of reactants may change the dynamics of the chemical reaction of [3]. The study of the reaction-rate  $Q(t)$  reflects this organization. For example, in  $d=1$  and from random initial conditions where  $Q$  starts from a maximum value, the reactive steady state is approached at an early stage via a slowing down of the reaction rate, as  $\sqrt{t}$ , as segregation into domains occurs. For desorption lower than a cross-over value  $p_c$  the growth of domains follows the same dynamics until the size of the system is reached and we get to a poisoned state for a time typically equal to the inverse of this cross-over desorption rate. The Euclidean dimension  $d=2$  is the marginal case and  $Q(t)$  has a complicated behaviour



**Figure 4.** Approach of the steady state from an initially saturated state. Reaction rate as a function of time for  $d = 1$  and  $L = 256$ . (●):  $p = 0.39 \times 10^{-2}$ , (x):  $p = 0.39 \times 10^{-3}$  and (○):  $p = 0.39 \times 10^{-4}$ . Solid line:  $Q = 4p\sqrt{\pi}/t$ .

as a result of the mesoscopic segregation. For  $d = 3$ , the reaction rate is constant for sufficiently large samples.

We believe that this general sort of behaviour is more general than the model in [1]. For example, in the simulations of Meakin and Scalapino [8] similar effects were found for the case where desorption is absent and poisoning always occurs. Experimental verification of these effects would be extremely interesting.

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