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## Kinetics of a monomer–monomer model of heterogeneous catalysis

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**Abstract.** The kinetics of an irreversible monomer–monomer model of heterogeneous catalysis is examined. In this model, two reactive species, A and B, adsorb and stick to single sites of a catalytic substrate. Surface reactions are assumed to occur only between dissimilar species which are nearest neighbours on the substrate. The kinetics of the process is studied in the reaction-controlled limit, where the adsorption occurs readily so that the process is limited by the reaction rate. We map the monomer–monomer model of heterogeneous catalysis on to a kinetic Ising model and solve the model exactly in one dimension, where the dynamics turns out to be a superposition of zero-temperature Glauber spin flip dynamics and infinite-temperature Kawasaki spin exchange dynamics. Finally, we discuss the monomer–monomer processes with desorption.

### 1. Introduction

Heterogeneous catalysis is a kinetic process of considerable interest in many unrelated fields of science and technology. In this process, the rate of a chemical reaction is enhanced by the presence of a suitable catalyst material [1]. Typically, such processes are described by Langmuir–Hinshelwood kinetics, where the molecules are assumed to be randomly distributed on the surface [1]. These are assumptions of a mean-field character, as microscopic details, such as spatial fluctuations in concentration and excluded volume interactions, are neglected. However, recent studies suggest that fluctuations are a crucial element in driving the kinetics [2].

Therefore, investigations of microscopic models have begun to identify the general principles underlying the kinetics of catalysis [3–10]. Results from computer simulations have shown that the phenomenon of ‘poisoning’ or saturation, where the catalytic substrate eventually becomes covered by one of the species only, occurs, thereby terminating the catalysis process, or there may be an apparent reactive steady state. Phase transitions which demarcate these possibilities are examined in a number of recent studies [3–12].

In this paper, we consider the monomer–monomer catalytic process. In this model, two reactive species, A and B, adsorb and stick to single sites of a catalytic substrate. Surface reactions are assumed to occur only between dissimilar species which are nearest neighbours on the substrate. For unequal adsorption probabilities, the substrate quickly becomes saturated with the preferred species. For equal adsorption probabilities, a finite substrate still becomes saturated, but at a much slower rate with equal probability of saturation by either of the two species.

There are two basic limiting cases of catalysis. When the reaction on the substrate occurs quickly, the process is limited by the adsorption rate. On the other hand, in the reaction-controlled limit the adsorption occurs readily so that the overall process

is limited by the conversion of unlike monomers to AB pairs. Much of the previous work [3-8, 10-12] has considered the adsorption-controlled limit. However, many catalytic processes occur in the opposite limit [1].

In the present paper, we focus on the reaction-controlled limit first studied in [13]. For the monomer-monomer model in the reaction-controlled limit, Monte Carlo simulations [9] and exact results [14] show that the basic dynamical features of the process agree with mean-field predictions when the dimensionality  $d$  of the substrate is at least 2, i.e. the upper critical dimension is  $d_c = 2$  [9] (for the monomer-dimer processes, an analogy to Reggeon field theory suggests that  $d_c = 4$  [11, 12]). It is therefore natural to study the kinetics of the monomer-monomer model at  $d = 1$ . In the following, we solve this model analytically and confirm that fluctuations indeed govern the long-time behaviour of the model in one dimension.

It is important that for the monomer-monomer processes only a quantitative difference between the reaction-controlled and adsorption-controlled limits has been observed [9, 15]. Thus the relatively simple reaction-controlled limit gives an insight into the general case of arbitrary adsorption and reaction rates.

The rest of this paper is organized as follows. In section 2 we map the monomer-monomer model on to a kinetic Ising model with competing dynamics. In section 3 we calculate one- and two-spin correlation functions. In section 4 we solve the catalysis model with desorption, and in section 5 we conclude the paper.

## 2. Dynamics

In the reaction-controlled limit, the substrate quickly becomes full. Thus, we start our study with a substrate that is randomly filled by equal amounts of As and Bs. If two neighbouring sites are occupied by opposite species, a reaction occurs in which the reactants desorb, each unoccupied site then being immediately refilled by either A or B with equal probability. For unequal adsorption probabilities, there is a net bias of either As or Bs, and the substrate becomes saturated exponentially in time with the preferred species.

We shall discuss the more interesting case of equal adsorption probabilities, where diffusive fluctuations drive the system to saturation. It is useful to map the model on to a kinetic Ising model. Identifying As with  $+1$  and Bs with  $-1$ , a full substrate may be described in terms of Ising variables  $S = \{S_k\}$ . It can be seen that the probability distribution  $P(S, t)$  of the Ising state  $S$  at time  $t$  satisfies the following master equation:

$$\begin{aligned} \frac{d}{dt} P(S, t) = & \sum (U_k(S^k) P(S^k, t) - U_k(S) P(S, t)) \\ & + \sum (V_k(S^{k,k+1}) P(S^{k,k+1}, t) - V_k(S) P(S, t)). \end{aligned} \quad (1)$$

In this equation,  $U_k(S)$  and  $V_k(S)$  denote the rates for the system to jump from the state  $S$  to the state  $S^k$  and  $S^{k,k+1}$ , respectively, where  $S^k(S^{k,k+1})$  are obtained from  $S$  by flipping the  $k$ th spin ( $k$ th and  $(k+1)$ th spins). These flip rates are given by the expressions

$$U_k(S) = \frac{1}{4\tau_1} [2 - S_k(S_{k-1} + S_{k+1})] \quad (2a)$$

$$V_k(S) = \frac{1}{4\tau_2} (1 - S_k S_{k+1}). \quad (2b)$$

Notice that the process (2a) defines the single-flip dynamics at zero temperature because the noise is absent as is evident from the fact that single-flip reactions  $AAA \Rightarrow ABA$  and  $BBB \Rightarrow BAB$  are impossible. Furthermore, the rate of the single-flip process  $ABA \Rightarrow AAA$  exceeds the rate of the process  $ABB \Rightarrow AAB$  by a factor of 2, since the former reaction proceeds after desorption of an arbitrary reaction pair (AB or BA) while the latter reaction proceeds after desorption of the only reaction pair. Thus the single-flip part of the surface catalytic process is actually given by the reaction rule (2a), introduced by Glauber in the realm of the kinetic Ising model [16]. Similarly, equation (2b) describes the spin-exchange dynamics (the Kawasaki dynamics) at infinite temperature because the exchange process does not depend on the neighbouring sites. A simple analysis shows that the dynamics of our model coincides with the spin dynamics (2) under the following constraint between the time-scales of spin-flip and spin-exchange processes:

$$\tau_1 = \tau_2. \quad (3)$$

Notice that the general case of arbitrary spin flip and spin exchange time-scales can also be dealt with.

It is known that the limiting regimes of zero-temperature Glauber dynamics and infinite-temperature Kawasaki dynamics are solvable (see [16, 17], respectively). When both spin flip and spin exchange processes are present, we have a non-equilibrium model since the system is in contact with two heat baths which are at zero and infinite temperature. As we shall show below, this model is also solvable in the sense that the time evolution of the one- and two-spin correlation functions can be calculated exactly. In closing we note that our model is an example of Ising-type systems with competing dynamics which have been investigated in a series of recent studies (e.g. see [18, 19] and references therein).

### 3. Analytical results for correlations

The advantage of the spin formulation of the problem is that one can easily derive a closed set of differential equations for the spin correlation functions

$$\langle S_i \dots S_j \rangle = \sum_S S_i \dots S_j P(S, t). \quad (4)$$

Consider first one-spin correlation functions. Multiplying both sides of equation (1) by  $S_k$  and summing over all configurations  $S$  we find that the average values of magnetizations at different sites,  $\langle S_k \rangle$ , are related by the following set of differential equations:

$$2\tau \frac{d}{dt} \langle S_k \rangle = \langle S_{k-1} \rangle + \langle S_{k+1} \rangle - 2\langle S_k \rangle. \quad (5)$$

Here we have introduced a renormalized time-scale  $\tau$ :

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2}. \quad (6)$$

A remarkable feature of the system (5) is that it coincides with the corresponding equations for the single-flip Glauber model [16], again at zero temperature but with

different time-scale  $\tau$ . Henceforth, we shall take this time-scale to be unity. Solving equations (5) at arbitrary initial conditions,

$$\langle S_k \rangle(t=0) = \sigma_k \quad (7)$$

yields (see [16])

$$\langle S_k \rangle = \exp(-t) \sum_{m=-\infty}^{\infty} \sigma_m I_{k-m}(t) \quad (8)$$

where  $I_m$  denotes modified Bessel functions.

We now consider two-spin correlation functions. After some algebra one finds for  $|i-j| \geq 2$ :

$$2 \frac{d}{dt} \langle S_i S_j \rangle = \langle S_{i-1} S_j \rangle + \langle S_{i+1} S_j \rangle + \langle S_i S_{j-1} \rangle + \langle S_i S_{j+1} \rangle - 4 \langle S_i S_j \rangle. \quad (9a)$$

These equations are identical to the corresponding equations of the Glauber model. The equations for  $|i-j| = 1$ , however, are different:

$$2 \frac{d}{dt} \langle S_k S_{k+1} \rangle = 2X + \langle S_{k-1} S_{k+1} \rangle + \langle S_k S_{k+2} \rangle - 2(1+X) \langle S_k S_{k+1} \rangle. \quad (9b)$$

In equations (9b) we have introduced the shorthand notation  $X = \tau_2 / (\tau_1 + \tau_2)$ . We shall investigate the general case of arbitrary  $X$ , i.e.  $0 \leq X \leq 1$ , although the constraint (3) gives the appointed value  $X = \frac{1}{2}$ .

Turn now to the transient kinetics of the system on the basis of the simplifying assumption that the initial distribution  $P(S, t)$  is translationally invariant. Then  $\langle S_i S_j \rangle$  depends on  $j-i$  at all times. Introducing  $R_n = \langle S_i S_{i+n} \rangle$  we can rewrite equations (9a) and (9b) as

$$\frac{d}{dt} R_n = R_{n-1} + R_{n+1} - 2R_n \quad \text{for } n > 1 \quad (10a)$$

$$\frac{d}{dt} R_1 = R_2 - (1+X)R_1 + X. \quad (10b)$$

One can easily find the steady state  $R_n = 1$  for all  $n \geq 1$ , which corresponds to the saturation. For arbitrary initial data the general solution is then constructed as a sum,

$$R_n(t) = 1 + \sum_{s=1}^{\infty} (R_s(0) - 1) Q_{ns}(t) \quad (11)$$

where  $Q_{ns}(t)$  are described by the equations

$$\frac{d}{dt} Q_{ns} = Q_{n-1,s} + Q_{n+1,s} - 2Q_{ns} \quad \text{for } n > 1 \quad (12a)$$

$$\frac{d}{dt} Q_{1s} = Q_{2s} - (1+X)Q_{1s} \quad (12b)$$

with initial conditions

$$Q_{ns}(t=0) = \delta_{ns}. \quad (12c)$$

A solution of equations (12a)-(12c) has been found recently in the context of a biophysical problem [20]:

$$Q_{ns}(t) = e^{-2t} \left( I_{n-s}(2t) - I_{n+s}(2t) + t^{-1} \sum_{k \geq 0} (-X)^k I_{n+s+k-1}(2t) \right). \quad (13)$$

In the present problem, with the initial state of the form  $R_n(0) = 0$ , a tedious but straightforward calculation yields the final expression for the two-spin correlation functions:

$$R_n(t) = 2e^{-2t} \left( \frac{X}{1+X} (I_n(2t) + I_{n+1}(2t)) + \sum_{p=n+1}^{\infty} I_p(2t) + \frac{1-X}{2} \sum_{k=0}^{\infty} (-X)^k I_{n+k}(2t) \right). \quad (14)$$

In deriving equation (14), we have used the recursion relation for the Bessel functions [21]

$$I_{n-1}(2t) - I_{n+1}(2t) = \frac{n}{t} I_n(2t) \quad (15)$$

and the identities [21]

$$\sum_{p=-\infty}^{\infty} I_p(2t) = \exp(2t) \quad \sum_{p=1}^{\infty} p I_p(2t) = t(I_0(2t) + I_1(2t)). \quad (16)$$

One can obtain more compact formulae in the scaling region

$$n \gg 1 \quad t \gg 1 \quad y = n(4t)^{-1/2} = \text{finite}. \quad (17)$$

Using the asymptotic relation for the modified Bessel functions in this scaling region [21],

$$\exp(-2t) I_n(2t) \approx (4\pi t)^{-1/2} \exp(-y^2) \quad (18)$$

and replacing the first sum on the right-hand side of equation (14) by the integral, we arrive at the simple scaling formula

$$R_n(t) \approx \text{Erfc}(y) \quad (19)$$

where

$$\text{Erfc}(y) = 2\pi^{-1/2} \int_y^{\infty} dZ \exp(-Z^2).$$

At long times, equations (17) and (18) predict a power law growth of the length  $L_A(t)$  and  $L_B(t)$  of domains,  $L_A(t) = L_B(t) \approx t^{1/2}$ . It is natural because the essential mechanism for saturation is the diffusion of domain walls. On this basis one can conclude that a characteristic saturation time grows as  $N^2$  with system size  $N$ .

One can estimate this saturation time quantitatively. Let us consider a finite one-dimensional lattice with periodic boundary conditions. We again assume a translationally invariant initial state. The correlation functions are governed by equation (10a) when  $1 < n < N-1$ , equation (10b) when  $n = 1$  and

$$\frac{d}{dt} R_{N-1} = R_{N-2} - (1+X)R_{N-1} + X \quad (10c)$$

when  $n = N - 1$ . The solution of equations (10a)-(10c) can be expressed as a superposition of the steady state and normal modes having the form  $\exp(-\lambda t)Q_n$ , i.e.  $R_n = 1 + \exp(-\lambda t)Q_n$ . By inserting this expression into equations (10a)-(10c) one finds the system of linear equations,  $MQ = -\lambda Q$ , with  $Q = (Q_1, \dots, Q_{N-1})^T$  and

$$M = \begin{pmatrix} 1-X & 1 & 0 & \dots & & \\ 1 & 0 & 1 & 0 & \dots & \\ 0 & 1 & 0 & 1 & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ & & \dots & 0 & 1 & 0 & 1 & 0 \\ & & & \dots & 0 & 1 & 0 & 1 \\ & & & & & 0 & 1 & 1-X \end{pmatrix}$$

Following the standard methods of matrix diagonalization [22] the eigenvalues of the  $(N - 1) \times (N - 1)$  tridiagonal matrix  $M$  can be written as

$$\lambda = 2(1 - \cos \theta) \tag{20}$$

and the possible values of  $\theta$  are determined from the following two transcendental equations:

$$X - 1 = \frac{\sin(N\theta/2)}{\sin[(N-2)\theta/2]} \tag{21a}$$

$$X - 1 = \frac{\cos(N\theta/2)}{\cos[(N-2)\theta/2]} \tag{21b}$$

It can be shown that equations (21a) and (21b) have  $N - 1$  distinct solutions in the interval  $0 \leq \theta \leq \pi$ . Thus by solving these equations one finds all the eigenvalues of the matrix  $M$ .

The long-time relaxational behaviour is governed by the smallest eigenvalue  $\lambda_{\min} = 2[1 - \cos(\theta_{\min})]$ . A simple analysis shows that  $\theta_{\min}$  is a solution of equation (21a). In the most interesting case,  $N \gg 1$ , a straightforward calculation yields an asymptotic formula for  $\theta_{\min}$ :

$$\theta_{\min} = 2\pi N^{-1}(1 + C_1 N^{-1} + C_2 N^{-2} + C_3 N^{-3} + \dots) \tag{22}$$

where  $C_1 = (1 - X)/(1 - X/2)$ ,  $C_2 = C_1^2$  and  $C_3 = C_1^3 - \pi^2 C_1(1 - C_1)(2 - C_1)/3$ .

As a consequence, we find that characteristic decay time of the longest-lived mode  $T$  for a system of size  $N \gg 1$ , with periodic boundary conditions, is

$$T = (\lambda_{\min})^{-1} = \frac{1}{4\pi^2} N^2 - \frac{C_1}{2\pi^2} N + \left( \frac{C_1}{4\pi^2} + \frac{1}{12} \right) + C_1(1 - C_1)(2 - C_1)(4N)^{-1} + \dots \tag{23}$$

where  $C_1 = (1 - X)/(1 - X/2)$ , and  $C_1 = \frac{2}{3}$  under the constraint (3). Up to the finite-size corrections, the dependence  $T = N^2$  was first predicted by ben-Avraham *et al* [9] on the basis of numerical simulations and qualitative arguments.

**4. Catalysis model with desorption**

It is clear that the present model of monomer-monomer surface catalytic reactions is a gross oversimplification of the actual catalytic process. A more realistic treatment

should consider the effects of surface diffusion, desorption, finite adsorption and reaction rates, nearest-neighbour interactions, etc. Very recently, some of these effects have been included and studied numerically in the monomer–dimer model of catalysis (see [6]). We have not succeeded in solving such realistic models even on a one-dimensional substrate. However, if only the desorption process is taken into account, the monomer–monomer model proves to be solvable by our methods.

We shall consider the monomer–monomer catalytic process in the reaction-limited regime with desorption [23]. This process was investigated numerically and theoretically in the mean-field approximation. The model can again be mapped on to a kinetic Ising model. When a particle desorbs, the unoccupied site is then immediately refilled with an A or a B equiprobably, i.e. we get the additional noise spin flips. Therefore the dynamics of the process consists of nearest-neighbour spin exchanges with the previous rate (2b) and spin flips with the modified rate

$$U_k(S) = \frac{1}{4\tau_1} [2 - S_k(S_{k-1} + S_{k+1})] + \frac{1}{2\tau_3}. \quad (24)$$

Notice that the process (24) describes the single-flip dynamics at non-zero temperature [16].

It is not difficult to find a set of differential equations for magnetizations,

$$2\tau \frac{d}{dt} \langle S_k \rangle = \gamma (\langle S_{k-1} \rangle + \langle S_{k+1} \rangle) - 2\langle S_k \rangle \quad (25)$$

and to solve this system with general initial conditions (7):

$$\langle S_k \rangle = \exp(-t/\tau) \sum_{m=-\infty}^{\infty} \sigma_m I_{k-m}(\gamma t/\tau). \quad (26)$$

Here we have introduced a renormalized time-scale,

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \frac{1}{\tau_3} \quad (27)$$

and a spin flip parameter  $\gamma$ ,

$$\gamma = \tau \left( \frac{1}{\tau_1} + \frac{1}{\tau_2} \right). \quad (28)$$

A remarkable feature of equation (25) is that it coincides with the corresponding equation for the single-flip kinetic Ising model [16] at the temperature  $T_{\text{eff}}$  which is defined from the relation  $\gamma = \tanh(2J/T_{\text{eff}})$ , where  $J$  is the strength of the nearest-neighbour interactions in the Ising model.

We now turn to the two-spin correlation functions. On this level, the description of the system in terms of the single-flip model at the temperature  $T_{\text{eff}}$  breaks down, but corrections are rather trivial. For simplicity, we write the equations only for translationally invariant initial conditions:

$$\frac{d}{dt} R_n = \gamma(R_{n-1} + R_{n+1}) - 2R_n \quad \text{for } N-1 > n > 1 \quad (29a)$$

$$\frac{d}{dt} R_1 = \gamma R_2 - (1+X)R_1 + \gamma X \quad (29b)$$

$$\frac{d}{dt} R_{N-1} = \gamma R_{N-2} - (1+X)R_{N-1} + \gamma X. \quad (29c)$$



Here  $X = (1/\tau_1 + 1/\tau_3)(1/\tau_1 + 1/\tau_2 + 1/\tau_3)^{-1}$  and we shall take the time-scale  $\tau$ , defined now by equation (27), to be unity again. A general solution to these equations is a superposition of the steady state,

$$R_n = C\eta^n + D\eta^{-n} \quad (30)$$

and the normal modes having the form  $\exp(-2t + \lambda\gamma t)Q_n$ . Eigenvalues  $\lambda$  can be written as  $\lambda = 2 \cos \theta$  and the possible values of  $\theta$  are determined from the following two transcendental equations:

$$X - 1 = \gamma \frac{\sin(N\theta/2)}{\sin[(N-2)\theta/2]} \quad (31a)$$

$$X - 1 = \gamma \frac{\cos(N\theta/2)}{\cos[(N-2)\theta/2]}. \quad (31b)$$

By inserting equation (30) into the system (29) one finds the well known Ising's relation for  $\eta = \eta(\gamma)$ ,  $\eta = \gamma^{-1}[1 - (1 - \gamma^2)^{1/2}]$ , and tedious expressions for the constants  $C$  and  $D$ .

Let us first consider a system with a finite desorption probability, i.e. we assume that  $\tau_1 \approx \tau_3$ . Then  $\gamma < 1$  and a simple analysis shows that the steady state behaves as  $R_n \approx C\eta^n$  for  $n \ll N$ . Thus a correlation length  $\xi$ ,  $\xi = -1/\ln(\eta)$ , is finite as it follows from the explicit expression for  $\eta = \eta(\gamma)$  and we see that system relaxes to the steady state with equal amounts of As and Bs. The relaxation time of the longest-lived mode,  $T = 1/(2 - 2\gamma)$ , is finite.

We now turn to the more interesting case when the number of catalyst sites  $N$  tends to infinity and, simultaneously, the desorption probability tends to zero. Furthermore, we assume that the latter quantity scales with the former as  $\tau_3/\tau_1 \approx N^\alpha$  with some exponent  $\alpha > 0$ .

When  $\alpha < 2$ , a system relaxes to the steady state  $R_n \approx C\eta^n$ , with approximately equal amounts of As and Bs, after the relaxation time  $T = 1/(2 - 2\gamma) \approx N^\alpha$ . When  $\alpha > 2$ , a system relaxes to the trivial steady state  $R_n = 1$  and, consequently, saturation occurs. The saturation time is proportional to the square of the number of catalyst sites,  $T \approx N^2/4\pi^2$ .

Finally, we discuss the behaviour at the borderline,  $\alpha = 2$ . For such a case, one can recast equation (30) into the form  $R_n = \cosh(\chi y)/\cosh(y)$ , where  $y = (2n - N)/N$  and  $\chi$  is defined by the relation  $\chi = N(\tau_1/4\tau_3)^{1/2}$ . The relaxation time is now given by the formula  $T = N^2(4\pi^2 + 4\chi^2)^{-1}$ .

Thus our exact approach reproduces the occurrence of a noise-induced transition [23] from monostability at  $\alpha < 2$  to bistability at  $\alpha > 2$  in a model of heterogeneous catalysis with desorption.

## 5. Conclusions

We have presented exact results for the kinetic behaviour of the monomer-monomer model of heterogeneous catalysis at  $d = 1$  in the reaction-controlled limit. For equal adsorption probabilities, we have found that diffusive fluctuations eventually drive a finite-sized system to saturation in a time proportional to the square of the number of catalyst sites. Furthermore, finite-size corrections to the characteristic decay time were evaluated analytically. We have also confirmed the occurrence of a noise-induced bistability in a model of heterogeneous catalysis with desorption.

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