

Reaction limited catalytic reaction in one dimension

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LETTER TO THE EDITOR

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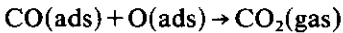
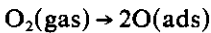
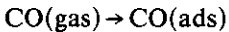
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Abstract. We analyse a mathematical model of reaction limited catalytic reaction on a one-dimensional lattice, which can be transformed into a system of random walkers with pair annihilation and spontaneous branchings. Time evolution of the correlation function and reaction rate are obtained theoretically and compared with numerical results.

Catalytic reactions have been attracting much attention from statistical physicists recently because of their peculiar characteristics due to their irreversible nature [1-8]. The oxidation of carbon monoxide on a platinum surface is one of the most typical catalytic reactions. The reaction follows the so-called Langmuir-Hinshelwood mechanism, that is



meaning that when a CO molecule adsorbed on a surface is close enough to O, they react forming a CO₂ molecule which diffuses from the surface, leaving two vacant sites.

Monomer-dimer models of heterogeneous catalysis first introduced by Ziff, Gulari and Barshad (ZGB) indicate the existence of dynamical phase transitions between the poisoned phase where all sites are covered by one species and the steady state where reactions continue forever [1, 9, 10]. The ZGB model is defined in the special case where the reaction occurs instantaneously (i.e. the adsorption limited case). The model has been generalized by Considine *et al* to allow a finite reaction rate and it has been shown that no steady state exists in the opposite limit, namely the reaction limited case [11].

In the case where two species are injected, both in the form of a monomer (monomer-monomer models), it is known that no steady state exists in one and two dimensions if the rate of spontaneous desorption is zero [12]. When desorption occurs with a finite rate we always have a steady state. A monomer-monomer model in the reaction limited case has been analysed theoretically by a mean-field approach [13, 14] and recently by solving the master equation in a rigorous manner [15].

In this letter we focus our attention on the time evolution of a one-dimensional catalytic surface in the reaction limited case including both monomer-monomer and monomer-dimer cases. We first show that the catalysis model can be transformed into a model of random walkers having a pair annihilating and branching nature identical to the branching annihilating random walk [16-18]. By solving the random walker model we derive a rigorous equation for the evolution of correlation function which

is essentially equivalent to that in [15]. We show that the system always converges to the poisoned state in the absence of spontaneous desorption. The decay of the total reaction rate follows either a power law, for equal injection of A and B, or an exponential for different injection rates. When spontaneous desorption occurs with a finite rate the steady state realizes with an exponentially decaying spatial correlation.

We consider a catalytic reaction on a one-dimensional discretized space and time. The initial condition is that two elements A and B are adsorbed on the lattice at random, and the time step is evolved by repeating the following two processes.

(1) The reaction process: a pair of sites is chosen randomly. If the pair is composed of different species the pair makes an AB molecule and desorbs leaving two vacant sites. In the other case nothing happens.

(2) The adsorption process: the vacant sites are occupied immediately by either A or B.

Since these two processes are carried out successively we can simplify the evolution rule by a replacement of AB (or BA) pair by either AA, AB, BA or BB with probabilities p , q , r and s , respectively ($p + q + r + s = 1$):

$$AB, BA \rightarrow \begin{cases} AA & \text{prob } p \\ AB & \text{prob } q \\ BA & \text{prob } r \\ BB & \text{prob } s. \end{cases}$$

In the case of independent monomer-monomer injection $p = p_A p_A$, $q = p_A p_B$, $r = p_B p_A$ and $s = p_B p_B$, where p_A (or p_B) denotes the probability of adsorbing an A (or B) molecule. When either A or B is injected in the form of dimers, then $q = r = 0$. So, our process allows monomer-monomer, monomer-dimer and dimer-dimer cases.

Let $Q_j(t) = 1$ (or -1) denote the state of site j being occupied by A (or B) at time step t . The configuration of the AB pair is expressed conveniently by introducing a new function $m_j(t)$ as

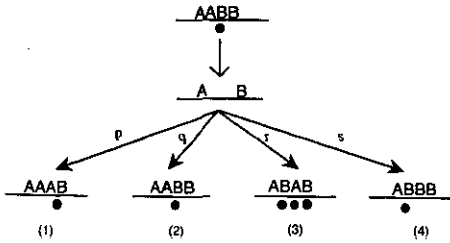
$$m_j(t) = \frac{1 - Q_j(t)Q_{j+1}(t)}{2}. \quad (1)$$

It is obvious that $m_j(t) = 1$ when the AB or BA pair is located on the j th and $(j+1)$ th sites, and $m_j(t) = 0$ otherwise. The number density of sites satisfying $m_j(t) = 1$, $P(m_j = 1, t)$, is considered to be proportional to the total reaction rate.

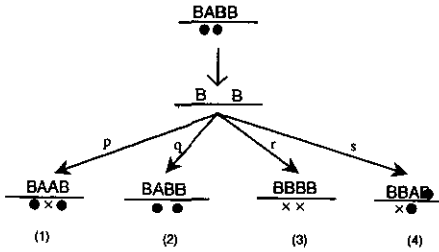
By regarding a pair AB or BA as an imaginary particle, the above catalysis model can be transformed into the following diffusion-reaction model of imaginary particles. Figure 1 illustrates the possible configurations after a reaction. Here an imaginary particle is denoted by \bullet . From this figure the evolution rules for the particles are given as follows.

(1) Choose a site randomly. Assume that we have found a particle at the j th site. The particle will either stay on the same site, hop onto the site $j+1$, hop onto the site $j-1$, or split into three particles on the sites $j-1$, j and $j+1$. The probability of each realization is q , p , s and r , respectively.

(2) Whenever two particles try to shear a site, they vanish immediately (see figure 1(b), branch (3)). Note that $\{Q_j(t)\}$ and $\{-Q_j(t)\}$ give the same configuration of imaginary particles, so the correspondence between $\{Q_j(t)\}$ and $\{m_j(t)\}$ becomes one-to-one by fixing the sign of a site in $\{Q_j(t)\}$. This set of evolution rules is identical to the branching annihilating random walkers.



(a)



(b)

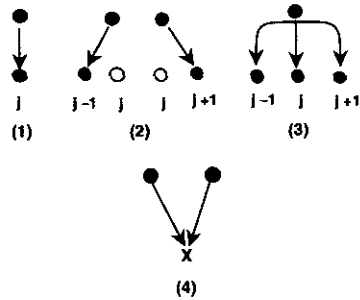


Figure 1. Illustration of the dynamics of configurations. Each event occurs with probability p , q , r and s , respectively. A solid circle indicates an imaginary particle. (b) (3) shows the case of pair annihilation.

Figure 2. Dynamics of an imaginary particle, composed of (1) staying on the same site, (2) diffusing, (3) branching and (4) annihilating.

The dynamics of $m_j(t)$ in a lattice of size N is given probabilistically as

$$m_j(t) = \begin{cases} m_j(t) & \text{prob } 1 - 2(p + s + r)/N \\ 0 & \text{prob } (p + s)/N \\ m_j(t) + m_{j-1}(t) \bmod 2 & \text{prob } (p + r)/N \\ m_j(t) + m_{j+1}(t) \bmod 2 & \text{prob } (s + r)/N \end{cases} \quad (2)$$

where the pair annihilation process is represented by the use of mod 2, and the boundary condition is periodic (see figure 2). From (2) it is obvious that we cannot obtain the probability of finding a particle at time step $t + 1$, $p(m_j = 1, t + 1)$, without the information for two bodies, $m_j(t) + m_{j-1}(t)$ and $m_j(t) + m_{j+1}(t)$. The same difficulty occurs for the two bodies, i.e. we cannot close the equation by two bodies. This is the usual trouble we encounter when we analyse multi-particle systems.

In order to treat this many-body effect rigorously we introduce the sum of k -bodies,

$$M_{j,k} \equiv m_j(t) + m_{j+1}(t) + \dots + m_{j+k-1}(t) \bmod 2 \quad (3)$$

which is equal to 1 (or 0) when the number of particles in the block is odd (or even). The time evolution of $M_{j,k}(t)$ is given as follows;

$$M_{j,k}(t) = \begin{cases} M_{j,k}(t) & \text{prob } 1 - 2(p + s + r)/N \\ M_{j-1,k+1}(t) & \text{prob } (p + s)/N \\ M_{j+1,k+1}(t) & \text{prob } (p + r)/N \\ M_{j+1,k-1}(t) & \text{prob } (s + r)/N. \end{cases} \quad (4)$$

Because the system is translationally invariant we can omit the j -dependence for statistical quantities such as probability of finding odd number of particles in a block of size k at time step t , $P_k(t)$. In the symmetric case of $p = s$ we can write down the evolution equation for $P_k(t)$ directly from (2) and (4).

$$P_1(t+1) = \left(1 - 2\frac{2p+r}{N}\right)P_1(t) + 2\frac{p+r}{N}P_2(t) \quad (5a)$$

and for $k \geq 2$,

$$P_k(t+1) = \left(1 - 4\frac{p+r}{N}\right)P_k(t) + 2\frac{p+r}{N}\{P_{k-1}(t) + P_{k+1}(t)\} \quad (5b)$$

with the boundary condition $P_N(t) = 0$.

The correlation function $C_k(t) \equiv \langle Q_j(t)Q_{j+k}(t) \rangle$ can be represented in terms of $P_k(t)$ simply as,

$$C_k(t) = 1 - 2P_k(t) \quad (6)$$

because $M_{j,k}(t) = 1$ (or -1) means $Q_j(t)Q_{j+k}(t) = -1$ (or $+1$). Substituting (6) into (5a), (5b), we have,

$$C_1(t+1) - C_1(t) = \frac{2}{N}[p - (2p+r)C_1(t) + (p+r)C_2(t)] \quad (7a)$$

and for $k \geq 2$,

$$C_k(t+1) - C_k(t) = \frac{p+r}{N}[C_{k-1}(t) - 2C_k(t) + C_{k+1}(t)] \quad (7b)$$

with the boundary condition $C_N(t) = 1$.

Equations (7a) and (7b) make a set of discretized diffusion equations in (k, t) -space. It is easy to show that the only stationary solution for $p \neq 0$ is $C_1 = C_2 = \dots = C_N = 1$, which means a poisoned state. In other words, we do not have the steady state.

The decay of the total reaction rate can be estimated in the following way. By taking a continuum limit with respect to r and t we get a diffusion equation,

$$\frac{\partial}{\partial t} C_k(t) = D \frac{\partial^2}{\partial k^2} C_k(t) \quad (8)$$

with the boundary condition $C_0(t) = 1$, where $D = 2(p+r)/N\Delta t$ is a diffusion constant. The solution of (8) is given for large t as

$$C_k(t) \cong 1 - \frac{k}{\sqrt{4Dt}}. \quad (9)$$

The total reaction rate is proportional to $P(m_j = 1, t)$,

$$P(m_j = 1, t) = \frac{1 - C_1(t)}{2} \cong \frac{N}{2} \frac{1}{\sqrt{4Dt}} \quad (10)$$

namely, it decays proportional to $t^{-1/2}$. This theoretical estimation can be confirmed numerically as shown in figure 3.

A poisoned state becomes unstable if we take the effect of spontaneous desorption into account. As we are considering the situation where adsorption takes place instantaneously, a desorption of molecule on the surface means a replacement of A (or B)

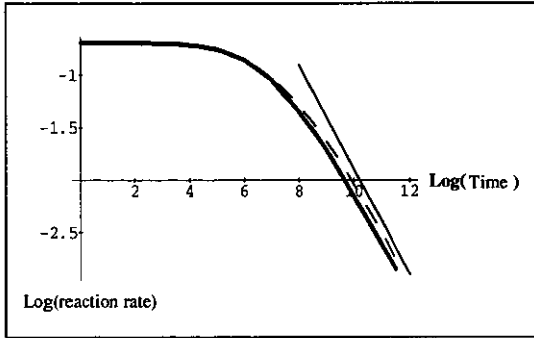


Figure 3. Numerical results for the symmetric adsorption rates with non-spontaneous desorption. The decay of the total reaction rate is plotted on a log-log scale: (1) $p = q = r = s = 0.25$ (solid curve), and (2) $p = 0.1, q = s$ and $r = 0.4$ (dashed curve). The slope of the line is $-\frac{1}{2}$. Here, the system size is 10^3 .

by B (or A). This process can be viewed as a spontaneous pair-creation of imaginary particles. Noting that the value of $Q_j(t)Q_{j+k}(t)$ is affected only when either $Q_j(t)$ or $Q_{j+k}(t)$ desorbs, we can readily have the equation for the correlation function with the replacement rate P_d as,

$$C_1(t+1) - C_1(t) = -\frac{4P_d}{N} C_1(t) + \frac{2}{N} \left(1 - \frac{P_d}{N}\right) [p - (2p+r)C_1(t) + (p+r)C_2(t)] \quad (11a)$$

and for $k \geq 2$,

$$C_k(t+1) - C_k(t) = -\frac{4P_d}{N} C_k(t) + \frac{2(p+r)}{N} \left(1 - \frac{P_d}{N}\right) [C_{k-1}(t) - 2C_k(t) + C_{k+1}(t)]. \quad (11b)$$

This set of equations is identical to that in [15] which is derived directly from the master equation.

The poisoned state solution $C_k(t) = 1$ (for $k = 1, 2, \dots, N$) is obviously not the stationary solution for (11a) and (11b), and the following exponentially decaying correlation is obtained by using the continuum limit approximation for $N \rightarrow \infty$:

$$C_k(t) = \exp(-k/k_c) \quad (12)$$

where the characteristic length k_c is given by

$$k_c = \sqrt{\frac{p+r}{2P_d}}. \quad (13)$$

Thus we have a steady state where A and B molecules are mixed, making clusters of size about k_c and the catalytic reaction continues forever. The steady state reaction rate is given as

$$P(m_j = 1, t) = \frac{1}{2} \{1 - \exp(1/k_c)\}. \quad (14)$$

This result shows a good agreement with simulations as demonstrated in figure 4.

Now we consider non-symmetric cases ($p \neq s$). Intuitively if $p > s$, then the surface will be quickly occupied by A and the clusters of B molecule will diminish monotonically on average. In this situation we have to distinguish the pair AB and BA by different imaginary particles because the imaginary particle for a AB pair has a tendency to

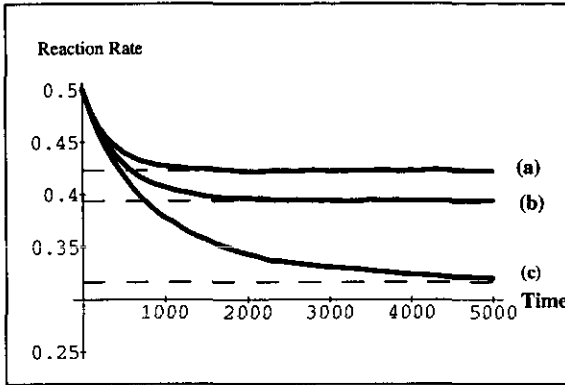


Figure 4. Numerical results for the decay of the total reaction rate in the case of $p = q = r = s = 0.25$ with (a) $Pd = 0.5$, (b) $Pd = 0.3$, (c) $Pd = 0.1$. Dashed lines show the theoretical values in the steady state.

move to the right and that of BA has a mean drift velocity to the left. The drift velocities for both directions are proportional to $|p - s|$. We cannot use the many-body technique here, so we assume an exponential decay for $p(m_j = 1, t)$ with the decay rate proportional to $|p - s|$ because the size of B-clusters distributes exponentially at the initial condition and the lifetimes of the clusters are proportional to their sizes on average:

$$P_k(m_j = 1, t) \propto \exp(-c|p - s|t) \tag{15}$$

where c is a constant. As shown in figure 5 this estimation gives good results for relatively large $|p - s|$. For smaller $|p - s|$ the decay shows an intermediate form between the power law, $t^{-1/2}$, and the exponential.

In conclusion, we analysed a one-dimensional reaction-limited catalysis model and derived the time evolution equation for the correlation function. In the absence of spontaneous desorption no active steady-state exists and the reaction rate decays monotonically following the power law, $t^{-1/2}$. When injection is non-symmetric we found an exponential decay in the reaction rate.

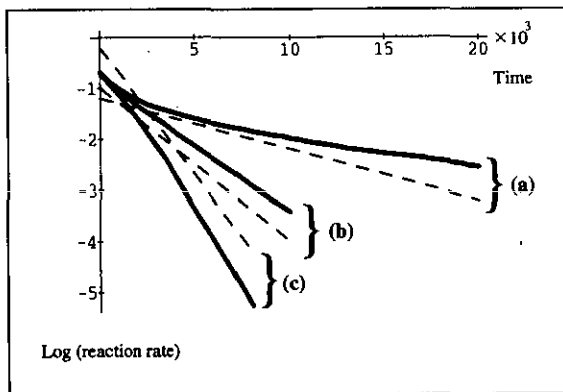


Figure 5. Numerical results for non-symmetric rates with no spontaneous desorption. The decay of reaction rate is plotted on a semilog scale. (a) $q = r = 0.25, p = 0.3, s = 0.2$ (b) $q = r = 0.25, p = 0.4, s = 0.1$ (c) $q = r = 0.25, p = 0.5, s = 0$.

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