LETTER TO THE EDITOR

Finite-size 'poisoning' in heterogeneous catalysis

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Abstract. The dynamics of a monomer–monomer and a monomer–dimer surface catalytic reaction is investigated. From the mean-field solution, finite systems eventually 'poison' at an exponential rate to a fully occupied, non-reactive state. For the monomer–monomer process, this poisoning is driven by concentration fluctuations of a diffusive nature, leading to poisoning times which vary as a power of the linear system size L. A comparison of the Monte Carlo simulations with the mean-field result suggests that the upper critical dimension for the monomer–monomer model is $d_c = 2$. For the monomer–dimer process, there is an effective potential that needs to be surmounted by fluctuations, leading to poisoning times which grow at least as fast as e^L. This gives rise to an apparent reactive steady state.

Heterogeneous catalysis is a fundamental kinetic process in which the rate of a chemical reaction is enhanced by the presence of suitable catalyst material [1]. A typical example is where reactants adsorb on a catalytic surface which then promotes the bonding of reactants. Once a reaction occurs, the reaction product desorbs, thereby allowing for continued operation of the system. This type of catalytic reaction underlies a host of technological processes and a substantial fraction of all chemical production [1].

It has only been very recently, however, that investigations of microscopic models have begun to identify the general principles underlying the dynamical behaviour of heterogeneous catalysis. Ziff *et al* [2] introduced a simple lattice model which appears to describe various features of the surface catalytic reaction of carbon monoxide (*monomers*, which adsorb onto a single lattice site) and oxygen (which are deposited as *dimers* and disassociate upon adsorption). Depending on the relative deposition rate of the monomers and dimers, there may be 'poisoning', where the surface eventually becomes covered by only one species, or there may be an apparent reactive steady state. Novel kinetic phase transitions demarcate these two possibilities. This intriguing behaviour has stimulated further work on this and a simpler monomer–monomer process to be defined below [3–7].

Our goal, in this letter, is to show that the mean-field solution, together with numerical simulations of very small systems, provide a rather complete description of the dynamics of idealised surface catalytic reactions. For the monomer–monomer process, we show that the final state of a finite system is always poisoned and that poisoning is approached at an exponential rate in mean-field theory. These facts are actually quite difficult to establish in numerical simulations of large systems [5].

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However, by extrapolating our numerical results from small systems, we can deduce the behaviour in the thermodynamic limit. Our simulations suggest that mean-field theory holds when the spatial dimension of the catalytic substrate is greater than or equal to 2. This value is identified as the upper critical dimension, d_c, of the monomer-monomer process. (Interestingly, for the monomer-dimer process, an analogy with Reggeon field theory [6] suggests that $d_c = 4$.) For the monomer-dimer process, we show that the putative reactive steady state is actually a transient phenomenon, and that the time for eventual poisoning varies exponentially in the system size. The origin of this long poisoning time stems from an effective bias away from the poisoned state due to the reaction process itself.

The monomer-monomer process consists of the following steps:

$$A + S \rightarrow A_S$$
$$B + S \rightarrow B_S \tag{1}$$
$$A_S + B_S \rightarrow (AB) + 2S.$$

Here S represents an unoccupied surface site and A_S and B_S denote A and B particles, respectively, adsorbed on the surface. In the deposition step, an A is chosen with probability p or a B is chosen with probability $q = 1 - p$. An attempt is then made to adsorb the chosen particle onto an arbitrary lattice site. If the site is already occupied, there is no adsorption and a new deposition is attempted, while if the site is unoccupied, adsorption occurs. After adsorption, if there happen to be AB nearest-neighbour pairs, then one such pair immediately bonds into an AB molecule which desorbs from the lattice, thus freeing two adjacent sites for subsequent adsorption.

We now derive the solution for the kinetics of this process in two versions of mean-field theory of increasing degree of applicability:

(i) *Complete graph.* For a complete graph of N sites (all pairs of sites connected) only A, or only B particles can exist at any time. The evolution of the system upon the attempted addition of a single particle can be represented by the stochastic process shown in figure 1. For a graph containing n A particles, the probability of no transition is n/N (i.e., deposition attempt on a previously occupied site), the probability of a step to the right is $p(1 - n/N)$ (corresponding to adsorption of an A), and the probability of a step to the left is $q(1 - n/N)$ (corresponding to B adsorption and subsequent AB desorption). The corresponding master equations are:

$$P_n(t + \Delta t) - P_n(t) = p\left(1 - \frac{|n-1|}{N}\right)P_{n-1}(t) + q\left(1 - \frac{|n+1|}{N}\right)P_{n+1}(t) - \left(1 - \frac{|n|}{N}\right)P_n(t) \tag{2}$$

for $|n| \leq N - 1$. Here we employ the convention that a graph occupied by nB's corresponds to the state $-n$. Since the transition probability out of a state is proportional to the number of empty sites in that state, the points $n = \pm N$ are *absorbing*, and the stochastic process terminates when it reaches either of these poisoned states. Thus
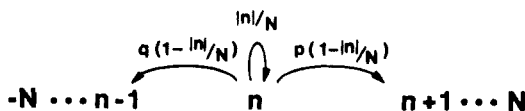

Figure 1. State space and transition probabilities of the monomer-monomer process on the complete graph. The sites $\pm n$ correspond to a graph occupied by n A, or n B particles, respectively.

similar equations hold for $|n| = N$, except for the modifications induced by $\pm N$ being absorbing. Note also that the physical time unit corresponds to $N\Delta t$, i.e. when one deposition has been attempted for each lattice site.

Several facts can now be deduced. Because of the existence of absorbing states, the final state of a finite system is always poisoned, and the probability that a finite system is not poisoned decreases exponentially in time, asymptotically [8]. If the system is initially empty, then for each stochastic 'path' which leads to poisoning of the system with all A's, there is a mirror image path which leads to poisoning of the system with all B's. From this fact, the first passage probability to $+N$ (poisoning to all A's) can be expressed as $p^N f_N(pq)$, where $f_N(x)$ can be computed for arbitrary N, while the first passage probability to $-N$ is $q^N f_N(pq)$. Consequently, the probability of eventual poisoning to all A's is

$$\mathcal{P}_A = \frac{p^N}{p^N + q^N}. \tag{3}$$

Because this argument depends only on the symmetry $p \leftrightarrow q$, $A \leftrightarrow B$, of the monomer-monomer process, (3) holds for any lattice of N sites.

Using generating function methods, we have computed the first-passage probability to arrive at either the A poisoned or the B poisoned state starting from an arbitrary initial state [9]. We thus confirm that the probability of not being poisoned decays exponentially in time. Moreover, for an initially empty system and for $p = q = \frac{1}{2}$, the mean poisoning time requires $2N^2 - N$ deposition attempts, i.e. $2N$ physical time units, asymptotically.

A better intuition for the monomer-monomer process can be obtained by passing to the continuum limit [8] to obtain the macroscopic rate equation for $\phi = \langle n \rangle / N$, the average fraction of occupied lattice sites (note that $\phi < 0$ means that the system is occupied by B's). By inspection, the rate equation is

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = (p - q)(1 - |\phi|). \tag{4}$$

In this equation, we make use of the relationship, $\langle |n| \rangle = |\langle n \rangle|$, which is valid when fluctuations are neglected. Equation (4) describes a Langmuir adsorption process, with poisoning to all A's (B's) for $p > \frac{1}{2}$ ($p < \frac{1}{2}$). For $p = q = \frac{1}{2}$, ϕ is stationary, and the fluctuations in ϕ become relevant. This leads to a diffusive process for $P_n(t)$ whose governing equation can be found by taking the continuum limit of the master equations. Defining $x = n/N$ and $P_n(t) = P(x, t)/N$, we obtain for $p = q = \frac{1}{2}$ (from equation (2)),

$$\frac{\partial P(x, t)}{\partial t} = \frac{1}{2N} \frac{\partial^2}{\partial x^2} (1 - x) P(x, t) \qquad 0 \leqslant x \leqslant 1. \tag{5}$$

To determine the appropriate boundary condition for the continuous equation, we reconsider the master equation, (2). For $n = N - 1$, in order that there is no hopping from N to $N - 1$, we require that the hopping probability $q(1 - |n + 1|/N)P_{n+1}(t)$ be zero. This yields the boundary condition $P(x = 1, t)$ is finite. We also use the fact that $P(x, t) = P(-x, t)$ for an initially empty system in restricting x to $[0, 1]$, and flux continuity at $x = 0$ also implies that $P(x, t)|_{x=0} = \partial P(x, t)/\partial x|_{x=0}$. Equation (5) describes the diffusion of the occupancy probability, with a state-dependent diffusion constant which vanishes linearly in the distance to the absorbing point.

To solve (5), we write the eigenfunction expansion

$$P(x, t) = \sum_\lambda a_\lambda p_\lambda(x) \exp\left(-\frac{\lambda^2}{8N} t\right) \tag{6}$$

and perform the transformation $q_\lambda(x) = (1-x)p_\lambda(1-x)$ to arrive at the standard form [9]

$$\frac{d^2}{dz^2} q_\lambda(z) + \frac{\lambda^2}{4z} q_\lambda(z) = 0 \tag{7}$$

with the corresponding boundary conditions $q_\lambda(z)|_{z=0} < \infty$ and $dq_\lambda(z)/dz|_{z=1} = 0$. Equation (7) has the general solution $q_\lambda(z) = A\sqrt{z}J_1(\lambda\sqrt{z}) + B\sqrt{z}\,Y_1(\lambda\sqrt{z})$, where J_1 and Y_1 are the Bessel and Neumann functions of order one, respectively. The boundary condition on q_λ gives $B = 0$, while the condition on q_λ' gives the eigenvalue λ_n as the nth zero of the Bessel function of order zero, J_0.

A plot of $P(x, t)$ at long times arising from this solution is shown in figure 2. In order to compare with data from finite-dimensional systems, we now identify x with $(n_A - n_B)/N$, where n_i is the number of particles of type i. Both the complete graph solution and the simulation data for a three-dimensional ($d = 3$) substrate show an enhancement of probability near the absorbing point. For the time dependence of the survival probability $S(t)$ (the probability that the system is not poisoned) we find numerically, that $S(t) \sim e^{-t/\tau}$ for $d \geq 2$, where $\tau \propto N$, as in the exact solution on the complete graph. For $d = 1$ there is a substantial time regime where $S(t) \sim t^{-1/2}$ before the asymptotic exponential decay sets in, and the mean poisoning time increases as N^2. These facts suggest $d_c = 2$ as the upper critical substrate dimension for the monomer–monomer process.

(ii) *Single-site mean-field theory.* A deeper insight into the monomer–monomer process is provided by positing that each lattice site coincides with the average environment [3]. This allows for the coexistence of A's and B's. Within this approach, we have derived the master equation for $P(n_A, n_B; t)$, the probability of having n_A A's and n_B B's at time t. More simply, the average concentrations of adsorbed particles,
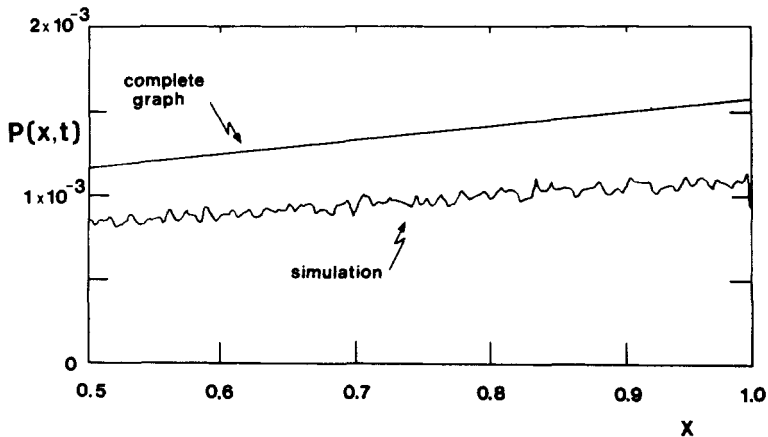

Figure 2. Plot of $P(x, t)$ for the complete graph at long times, together with simulation data for $P((n_A - n_B/N), t)$ for a three-dimensional ($d = 3$) simple cubic substrate with $N = 8^3$.

$x = n_A/N$ and $y = n_B/N$ respectively, evolve as

$$\frac{dx}{dt} = (1 - x - y)[p(1 - y)^{2d} - q(1 - (1 - x)^{2d})] \tag{8a}$$

$$\frac{dy}{dt} = (1 - x - y)[q(1 - x)^{2d} - p(1 - (1 - y)^{2d})]. \tag{8b}$$

The first term in $(8a)$ accounts for the adsorption of an A with no nearest-neighbour B's present, while the second term accounts for the loss of an A due to the deposition of a B with at least one nearest-neighbour A. When $p \neq q$, the system flows to a poisoned state in a time of order unity, while for $p = q = \frac{1}{2}$, there is a two-state evolution process (figure 3). First, there is a relatively rapid initial flow to the curve of fixed points $(1 - x)^{2d} + (1 - y)^{2d} = 1$, determined by $dx/dt = dy/dt = 0$. This corresponds to the initial filling of the system.
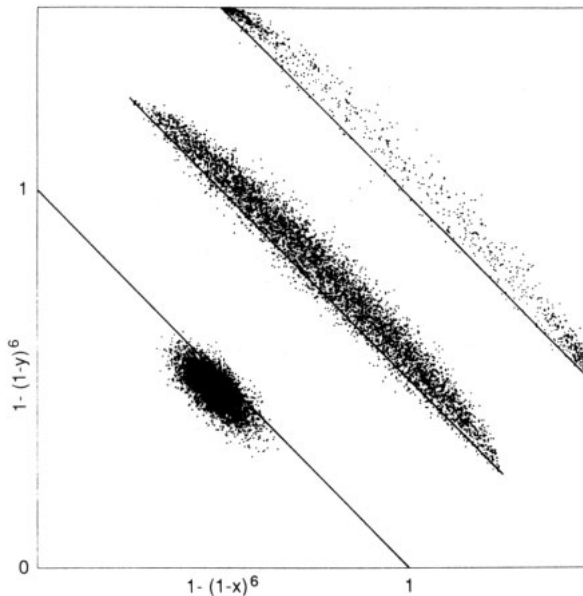

Figure 3. Evolution of an ensemble of initially empty $d = 3$ systems with $N = 11^3$ at various stages of the reaction process. Subsequent stages are shown offset. The straight line represents the curve $(1 - x)^6 + (1 - y)^6$.

Once the fixed curve is reached, only concentration fluctuations drive the system. This evolution can be determined from the master equation [9]. We find diffusive motion on the fixed curve, leading to the eventual poisoning of the system, in much the same manner as on the complete graph. In the limit $d \to \infty$, the fixed curve degenerates to the right-angle line segments consisting of the vertical and horizontal axes; this reproduces the solution on the complete graph. These mean-field predictions agree with numerical simulations for substrate dimensionality $d \geq 2$. For $d = 1$, the initial filling stage leads to essentially complete occupation, i.e. the fixed curve is now the line $x + y = 1$, and there is non-trivial interfacial dynamics between A-rich and

B-rich regions. This anomalous behaviour supports the assertion that $d_c = 2$ for the monomer–monomer process. The possibility that $d_c = 2$ would be a nice illustration of an upper critical dimension that can be realised in a physical system.

The phenomenologically richer monomer–dimer process [2] can be usefully analysed by an approach in the same spirit to that employed above. The monomer–dimer process consists of the following steps:

$$A_2 + 2S \rightarrow 2A_S$$
$$B + S \rightarrow B_S \tag{9}$$
$$A_S + B_S \rightarrow (AB) + 2S.$$

In the deposition step, an A_2 is chosen with probability p, or a B is chosen with probability $q = 1 - p$, and an attempt is made to adsorb the chosen molecule either onto a pair of nearest-neighbour sites (A_2), or onto a single site (B). If adsorption does occur, then if AB nearest-neighbour pairs are created, one such pair immediately bonds into an AB molecule which desorbs from the lattice.

Again, the states of being poisoned by all A's or by all B's are *absorbing*. Thus the apparent reactive steady state is actually a transient, albeit very long-lived, phenomenon in a finite size system. To determine the nature of this transient, consider the macroscopic rate equation for the monomer–dimer process on the complete graph (in analogy with (4)),

$$\frac{d\phi}{dt} = 2p(1 - |\phi|)^2 - q(1 - |\phi|). \tag{10}$$

For $p < \frac{1}{3}$ the system ultimately poisons to all B's, i.e. $\phi(t \rightarrow \infty) = -1$ unless the system is initially poisoned with all A's. However, for $p > \frac{1}{3}$, there is a stable non-trivial fixed point at $\phi^* = 1 - q/2p$ which is the attractor if $\phi(0) > -\phi^*$. The point ϕ^* is the reactive steady state for an *infinite* system in the mean-field limit. However, because the poisoned states are the only true absorbers, fluctuations will ultimately drive a finite system away from ϕ^* to the poisoned states. In the monomer–monomer process these
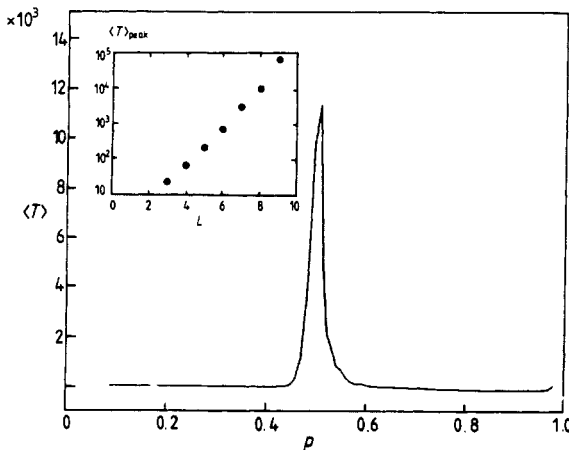

Figure 4. Plot of the mean poisoning time against the dimer deposition probability p for an 8×8 square substrate. The exponential variation of the peak value of the poisoning time with linear system size is shown in the inset.

fluctuations had to overcome only a state-dependent diffusion constant which vanished monotonically as the poisoned state is approached. However, in the monomer–dimer process these fluctuations must also overcome a potential 'well' induced by the presence of a stable fixed point, in order to reach poisoning. Thus while the mean poisoning time $\langle T \rangle$ increases as a power-law of the system size L for the monomer–monomer process, $\langle T \rangle$ increases at least as fast as e^L for the monomer–dimer process (figure 4). The anomalously long poisoning time manifests itself as the observed reactive 'steady-state' in simulations of large systems [2]. Analysis of this behaviour is also being performed by exploiting an analogy between the monomer–dimer process and directed percolation [10].

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