KINETICS OF LATTICE MODELS OF CATALYSIS

S. REDNER
Center for Polymer Studies and Department of Physics,
Boston University, Boston MA 02215.

INTRODUCTION

The kinetics of the monomer-monomer and the monomer-dimer catalysis models are discussed. In the monomer-monomer model, two reactive species, A and B, adsorb irreversibly onto single sites of a catalytic surface, and nearest-neighbor adsorbed AB pairs can bond to form a reaction product which desorbs. In the monomer-dimer model, one of species is diatomic, and requires two free lattice sites for adsorption. A complete-graph solution shows that finite systems eventually "saturate", *i. e.*, become completely covered by only a single species. For the monomer-monomer process, this saturation is driven by diffusive concentration fluctuations, and the saturation time increases linearly in the number of sites N. For the monomer-dimer process, there is an effective "potential" that needs to be surmounted by the fluctuations, leading to a saturation time which grows exponentially in N. This slow saturation gives rise to the apparent reactive steady state of the model.

We also discuss various aspects of the spatial arrangement of the reactants on a catalytic surface. The effect of the surface reaction is to introduce an effective repulsion between unlike species, leading to clustering. We discuss the kinetics of this cluster growth and related statistical properties of the growing clusters. We also consider the situation where a microscopic attractive interaction between adsorbed unlike species competes with the effective repulsion. This competition stabilizes a reactive steady state. Connections between catalysis models and interacting particle systems will also be mentioned.

THE MONOMER-MONOMER MODEL

The monomer-monomer model consist of two steps [1]: First there is adsorption of A's and B's, onto single unoccupied substrate sites at respective rates k_A and k_B, yielding the adsorbates, A_s and B_s. Secondly, when adsorbates of different species occupy nearest-neighbor substrate sites, they react at a rate k_r to form a product which desorbs, leaving two sites available for further adsorption. This process is represented by:

$$\begin{aligned} A + S &\xrightarrow{k_A} A_s \\ B + S &\xrightarrow{k_B} B_s \\ A_s + B_s &\xrightarrow{k_r} (AB)\uparrow + 2S. \end{aligned} \tag{1}$$

If $k_A, k_B \ll k_r$, the process is adsorption-controlled, and reaction-controlled in the opposite case. In the adsorption-controlled limit, if adsorption leads to a nearest-neighbor AB pair, then a reaction occurs where one pair bonds and desorbs from the substrate. In the reaction-controlled limit, adsorption occurs rapidly so that the substrate is always nearly full. If two randomly-chosen nearest-neighbor sites happen to be occupied by opposite species, a reaction occurs in which the reactants desorb, with each unoccupied site then being immediately refilled by either an A with probability p, or a B with probability q.

KINETICS ON THE COMPLETE GRAPH

To realize the mean-field limit, model the surface by an N-site complete graph where each site is "connected" to all other sites. On this graph, the spatial distribution of the reactants is irrelevant, and global densities suffice to describe the system. In the adsorption-controlled limit, the instantaneous reaction of AB pairs and the fact that all

sites are reactively connected forbids the coexistence of A's and B's on the surface. The system is characterized by $n \equiv n_A - n_B$, where n_A and n_B are the numbers of A and B adsorbates, respectively. The number difference n equals n_A, if the substrate contains only A's, and equals $-n_B$, if the substrate contains only B's. In an elemental event of adsorption (and possible surface reaction), n changes by $+1$ if an A is deposited, by -1 if a B is deposited, and changes by 0 if deposition is attempted onto a previously occupied site.

The hopping probabilities corresponding to these possibilities are

$$W(n \to n+1) = p\left(1 - \frac{|n|}{N}\right), \quad W(n \to n-1) = q\left(1 - \frac{|n|}{N}\right), \quad W(n \to n) = \frac{|n|}{N}. \tag{2}$$

If the surface becomes completely covered by a single species, $n = \pm N$, the hopping probabilities are identically zero, corresponding to saturation. Defining $P_n(t)$ as the probability that the substrate has n adsorbed reactants at time t, then $P_n(t)$ obeys the master equation

$$P_n(t+\Delta t) - P_n(t) = p(1 - \frac{|n-1|}{N})P_{n-1}(t) - (1 - \frac{|n|}{N})P_n(t) + q(1 - \frac{|n+1|}{N})P_{n+1}(t), \tag{3}$$

for $|n| \leq N-1$, while for $|n| = N$ slightly different equations apply to account for the absorbing boundary condition. For a catalytic surface with a constant external supply of reactants, a time unit corresponds to the time required for an adsorption attempt onto each surface site. Consequently, the time interval Δt for a single elemental event in the stochastic process is proportional to $1/N$.

Writing $x \equiv n/N$, with x ranging between -1 and $+1$ in steps of $1/N$, and defining the continuous probability $P(x,t)\,dx = \frac{1}{N}P_n(t)$ as $N \to \infty$, the probability density satisfies the Fokker-Planck equation,

$$\dot{P}(x,t) = (q-p)\frac{\partial}{\partial x}(1-|x|)\,P(x,t) + \frac{1}{2N}\frac{\partial^2}{\partial x^2}(1-|x|)\,P(x,t). \tag{4}$$

The diffusion coefficient is state dependent, $D(x) = (1-|x|)$, reflecting the probability of successful adsorption being proportional to the fraction of empty sites, $1-|x|$. The evolution of the surface concentration therefore can be viewed as the motion of a random walk moving in an absorbing interval that is increasingly "sticky" near the extremities. If the walk reaches the endpoints where $D = 0$, the walk sticks, corresponding to saturation. In a finite-size system, therefore, saturation must occur in a finite time, and the probability that the system has not yet saturated decreases exponentially in time, asymptotically. This saturation stems from the fluctuations due to the discreteness of a finite-size system when $p = q$.

The general solution to the Fokker-Planck equation in the interesting case of $p = q = \frac{1}{2}$ is

$$P(x,t) = \sum_{n=1}^{\infty} A_n \frac{J_1(j_{0,n}\sqrt{1-|x|})}{\sqrt{1-|x|}} \exp\left(-\frac{j_{0,n}^2}{8N}t\right), \tag{5}$$

where the A_n are fixed by initial conditions, and where $j_{0,n}$ is the n^{th} zero of the Bessel function of order 0. The resulting probability density has a cusp at the origin, which arises from the discontinuous first derivative in $D(x)$ at $x = 0$, and the probability density *increases* near the edges of the interval. The qualitative effect of the state-dependent diffusion coefficient is to increase the probability of the system being close to the saturated state and also to inhibit the ultimate saturation, relative to a constant diffusivity system.

From $P(x,t)$, the "survival" probability, $S(t) \equiv \int_{-1}^{+1} P(x,t)\,dx$, *i. e.*, the probability that the substrate has not saturated by time t, is $S(t) = \sum_n S_n \exp\left(-\frac{t}{\tau_n}\right)$, where

$\tau_n = 8N/j_{0,n}^2$ is the characteristic decay time of the $n^{\rm th}$ mode ($\tau_0 \approx 1.38N$, while for a constant diffusivity system $\tau_0 = 4N/\pi^2 \approx 0.405N$). A closely related quantity is the mean saturation time, *i. e.*, the mean-first passage time to reach $\pm N$ in the stochastic process. Denote the mean first-passage time as t_n when starting at site n, corresponding to a substrate which initially contains n A's. Then t_n obeys the recursion relation,

$$t_n = \frac{1}{2}(1 - \frac{n}{N})(t_{n-1} + \Delta t) + \frac{1}{2}(1 - \frac{n}{N})(t_{n+1} + \Delta t) + \frac{n}{N}(t_n + \Delta t). \qquad (6)$$

Taking the continuum limit this recursion relation and using $\Delta t = 1/N$, one finds the solution

$$t(x) = 2N(1-x)(1 - \ln(1-x)). \qquad (7)$$

where $t(x)$ now denotes the first-passage time to ± 1, starting from an initial surface coverage $x = n/N$. Thus the mean saturation time grows linearly in N for $x \approx 0$ (a nearly empty system), and there is a logarithmic dependence for $|x| \approx 1 - 1/N$ (a nearly full system).

To summarize, the complete graph solution is equivalent to a hindered diffusion process on a one-dimensional absorbing interval. This equivalence provides a useful intuitive picture for the kinetics of the monomer-monomer model. In the mean-field approach, saturation of the surface, corresponding to absorption at the endpoints in the underlying diffusion process, occurs in a time which is proportional to N. The probability of not being saturated decays exponentially at long times. These features are observed in simulations of two- and higher-dimensional substrates.

CLUSTERING IN THE MONOMER-MONOMER MODEL

When the monomer-monomer process takes place on a surface of finite spatial dimensionality, the reaction between unlike species leads to an effective repulsion between unlike species. Consequently, there is a natural tendency for particles of the same species to cluster into domains of ever-increasing size. In one dimension, this clustering can be understood on the basis of the close analogy between the behavior of the motion of domain walls and diffusive annihilation processes in one dimension. Thus the average domain size grows as $\sqrt{t}$, and the distribution of domain sizes is expected to be sharply peaked. On the other hand in two dimensions, the number of clusters of s-sites, $n_s(t)$ varies as $s^{-\tau}$, with $\tau \approx 1.95$, over many decades is s [2]. Furthermore, the typical cluster size grows linearly in time. The origin of these power-law behaviors is not clear. The clustering and concomitant linear growth of the typical cluster size is the feature that leads to a saturation time which grows as a power of the system size.

These properties of the size distribution are closely analogous to clustering phenomena in the *voter model* [3]. This is an interacting particle system in which each site of a lattice contains an A or a B, and the state of each site can change at a rate proportional to the number of neighboring sites which are in the opposite state. One one and two dimensions, it has been proved that the voter model "clusters", in a manner analogous to the monomer-monomer model. The nature of the cluster size distribution in three dimensions has not yet been addressed fully.

THE MONOMER-DIMER AND INTERACTING MONOMER-MONOMER MODEL

The phenomenologically richer monomer-dimer process can be usefully analyzed by an approach in the same spirit to that employed above. The monomer-dimer process consists of the following steps [4]:

$$\begin{aligned} A_2 + 2S &\to 2A_S \\ B + S &\to B_S \\ A_S + B_S &\to (AB)\uparrow + 2S. \end{aligned} \qquad (8)$$

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-neighbor sites (A_2), or onto a single site (B). If adsorption does occur, then if AB nearest-neighbor pairs are created, one such pair immediately bonds into an AB molecule which desorbs from the lattice.

Again, the states of being saturated 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 number difference n in the monomer-dimer process on the complete graph

$$\frac{dn}{dt} = 2p(1 - |n|)^2 - q(1 - |n|). \tag{9}$$

For $p < \frac{1}{3}$ the system ultimately saturates to B's, $n(t \to \infty) = -1$, unless the system is initially saturated with all A's. However, for $p > \frac{1}{3}$, there is a stable non-trivial fixed point at $n^* = 1 - \frac{q}{2p}$ which is the attractor if $n(0) > -n^*$. The point n^* is the reactive steady state for an *infinite* system in the mean-field limit. However, because the saturated states are the only true absorbing points, fluctuations will ultimately drive a finite system away from n^* to the saturated states. This can be seen by an analysis of the master equation which can be written in the same spirit as Eq. (3). In the monomer-monomer process these fluctuations had to overcome only a state-dependent diffusion constant which vanished monotonically as the saturated 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 saturation. Thus while the mean saturation time increases as a power-law of the system size N for the monomer-monomer process, increases as e^N for the monomer-dimer process. The anomalously long saturation time manifests itself as the observed reactive "steady-state" in simulations of large systems.

It is also possible to stabilize an apparent reactive steady-state in the monomer-monomer model by introducing energetic interactions between adsorbates which compete with the reaction-induced repulsion between unlike species. For example, suppose that whenever a particle is deposited in a small unoccupied region, it moves preferentially next to a site containing the opposite species. This simple construction turns out destabilize the tendency for growth of large single-species domains. Consequently, the concentration fluctuations that lead to saturation are damped out. We find that the saturation time for this system can grow faster than a power-law in the system size. Further properties of this type of interacting system are under investigation.

We gratefully acknowledge grant #DAAL03-89-K-0025 from the Army Research Office for partial support of this research.

REFERENCES

1. D. ben-Avraham, S. Redner, D. Considine, and P. Meakin, J. Phys. A 23, L613 (1990); D. ben-Avraham, D. Considine, P. Meakin, S. Redner, and H. Takayasu, J. Phys. A 23, xxxx (1990).

2. R. M. Ziff and K. Fichthorn, Phys. Rev. B 34, 2038 (1986); S. Redner (unpublished).

3. R. Durrett, Lecture Notes on Particle Systems and Percolation, (Wadsworth & Brooks/Cole, Pacific Grove, CA, 1988).

4. R. M. Ziff, E. Gulari, and Y. Barshad, Phys. Rev. Lett. 56, 2553 (1986).