

Statistical Models for Surface Catalysis: Evidence for Anomalous Reaction Rates

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We consider two elementary models for reaction kinetics on a catalytic surface: a monomer–monomer model and a monomer–dimer model. In both cases we use Monte Carlo simulations to exhibit anomalous reaction kinetics which is the expression of density fluctuations and self-organization of reactants in the system. We show the influence of this self-organization on the macroscopic behavior of the system.

Catalytically activated processes have been known for a very long time now but still present a challenge for fundamental research. Recently, statistical physics concepts have been used to describe collective phenomenon in catalysis such as pattern formation in excitable media¹ or nonequilibrium phase transitions.^{1,2} For example, a great deal of work has been done on pattern formation associated with nonlinear effects [see, for example, refs 4 and 5 and references therein].

In a reaction process, one of the sources of nonlinearity is the order of the reaction rate or some nonlinear adsorption/desorption process. The simple theory of reaction kinetics shows that the reaction rate should always be considered as the product of reactant densities entering the reaction.⁶ This defines a differential equation (the rate equation) for the reactant dynamics or the steady-state densities. The rate constant, the coefficient of proportionality between the reaction rate and the reactant product, is the expression of local dynamics. It is proportional to the hopping rate if the process is diffusion limited or to a reaction frequency when it is reaction limited. Thus a clear-cut separation exists between local variables that could be derived, for example, from quantum mechanics and collective variables expressed in the most simple way as the product of concentrations.

Until recently, this theory was considered to be firmly established. However, in the case of diffusion-limited reactions the simple picture was shown to be inadequate for the decay rates of several elementary reactions such as the trapping problem, the $A + A \rightarrow 0$ and the $A + B \rightarrow 0$ processes [for example, see reviews in ref 7 and ref 8 and refs therein]. More recently, anomalous results were found also in steady-state situations.^{9,10} It became clear that simple reaction laws are insufficient to account for the key role of fluctuations. Macroscopic results depend on the Euclidean dimension of the medium, and anomalous decay forms or effective orders of reaction were found. Moreover, fractal structures¹¹ have been considered to account for spatial disorder. In this case as well, fluctuations are prevalent and influence the macroscopic picture.^{7,8} In general, anomalous laws are the result of self-organization of reactants that can lead to spatial pattern formation.^{2,13}

In this paper we will show in two simple examples how reaction anomalies occur in catalytic models and how they are related to some more complex properties of the system such as coexistence diagrams, out-of-equilibrium phase transitions, and wave propagation. These processes are not necessarily diffusion limited.

The work we present here is the result of Monte Carlo simulations which incorporate internal fluctuations in a natural way.

The first elementary process we consider is a monomer–monomer catalytic process, $A + B \rightarrow 0$, with a high adsorption rate and desorption. No diffusion of reactants is allowed. A symmetric form of this process was first proposed by Fichthorn Gulari and Ziff³ (FGZ). We consider the case when the species are not symmetric in adsorption and desorption. We find self-organization and exhibit the phase diagram of species A and B, which depends on the geometry. The second model studied is the monomer–dimer model, $A + B_2 \rightarrow 0$, for catalysis on a surface introduced by Ziff, Gulari, and Barshad² (ZGB). This model exhibits a first-order out-of-equilibrium phase transition. We monitor the reaction rate in the vicinity of the transition, and we also show that a spatial self-organization of the reactants is responsible for anomalous reaction kinetics.

Bimolecular Reaction Rate and Organization of Reactants

The reaction rates for a diffusion-limited reaction in 3D was derived by Smoluchowski,¹⁴ who related the gradient of the pair correlation function to the rate of reaction Q_{AB} . In an average particle reference frame, the number of reactions is the flux of particles diffusing through the reaction surface Σ (considered here as a sphere). Thus,

$$Q_{AB} = \Sigma D [\nabla m_{AB}(r)]_{r=a} \quad (1)$$

where a is a microscopic-size radius of the reaction sphere and $m_{AB}(r)$ is the two-particle correlation function. There is a natural length scale Λ that expresses roughly the typical distance between an A and a B. We can write

$$Q_{AB} = \Sigma D \frac{\rho_A \rho_B}{\Lambda} \quad (2)$$

The length scale Λ is the scale of segregation indicating the typical size of A and B clusters. In a standard picture,^{6,14} Λ is of the order of the microscopic-size a and thus the reaction rate is

$$k_{\text{classical}} \approx \Sigma D / a \approx a^d / \tau \quad (3)$$

where τ is a microscopic hopping rate. For a reaction-limited equation, the reaction rate has also the same dimensional form but the time τ is a typical reaction time and a^d a microscopic reaction volume. The classical relation holds as well when a vigorous mixing is applied to the reactants and when, at any time, the distribution of particles can be considered to be Poissonian.¹⁵ Thus in all these cases, the order of reaction is 2.

Nevertheless, in disordered materials like glasses, important deviations from classical reaction rates have been found due to

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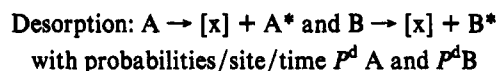
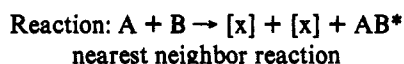
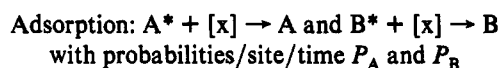
long-range or hierarchical interactions between species.⁷ In numerous other cases, the rate "constant" was shown to vary when spatial fluctuations organize the substrate. An effective order of reaction larger than 2 may possibly occur.^{8,10,12} In the following, we use as an indicator of local self-organization the effective segregation length:

$$\Lambda = \frac{\rho_A \rho_B}{Q_{AB}} \quad (4)$$

Note the important point that an excess of A in B (respectively of B in A) is not an indicator of segregation but of another phenomenon called saturation.^{3,13,14} An equation like (4) will be able to discriminate between both effects. Note that for diffusion on a regular lattice we have in general $\sum D \cong 1/\tau$ and that eq 4 applies as well to situations where no diffusion is present a priori in the system (reaction limited).

Monomer–Monomer Catalysis

Let us now consider a classical Langmuir–Hinshelwood reaction involving two different species A and B adsorbed on a catalytic surface. There is no diffusion involved. The reaction scheme follows three steps:



The symbol "*" means a species in the gas phase, and "[x]" means a free site. We suppose that reaction is slow compared to adsorption so that empty sites on the lattice are rare. To parametrize possible dissymmetry between A and B, we introduce a set of three variables (x, y, p) such that

$$P_A = (1 - x)/2, P_B = (1 + x)/2$$

$$P^d_A = p(1 + y)/2, P^d_B = p(1 - y)/2 \quad (5)$$

This is a dissymmetric version of the model originally proposed by FGZ,³ who take $x = y = 0$. A mean-field solution was given by Redner and Tayakatsu¹⁶ and an exact solution by Clément, Leroux-Hugon, and Sander¹⁷ on any Euclidean lattice. An extension of the solution to disordered lattices has been proposed by Clément, Leroux-Hugon, and Argyrakis.¹⁸ The monomer–monomer model has also been considered by Evans,¹⁹ and the dynamical aspect was stressed [see also refs 20 and 21].

In Figure 1a and 1b we show the result of a Monte Carlo simulation for the steady-state distribution of reactants on a 2d lattice for $x = y = 0$ (FGZ model) with desorption $p = 10^{-3}$. The distribution of reactants is initially random (Figure 1a), but after 10 000 steps, an obvious segregation between particles occurs. In Figure 2a and 2b the simulation was done on a fractal percolation cluster [on percolation theory, see ref 22]. The segregation phenomenon is even more obvious (here $x = y = 0, p = 10^{-4}$). Clément et al.^{17,18} have shown that, in general, when p goes to zero, one can write the reaction rate in the form

$$Q \approx p^{1-d_s/2} \quad (6)$$

where d_s is the spectral dimension of the lattice. On a percolation cluster we have $d_s = 4/3$.²² Equation 6 is valid only for $d_s < 2$. At $d_s = 2$, we have a marginal behavior.¹⁷ Since the lattice is full, we have, in the limit of infinite lattice size, a segregation

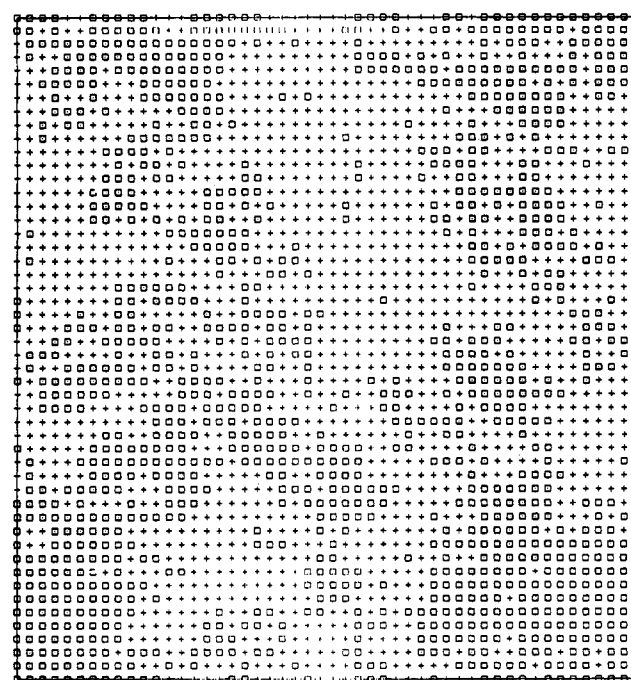
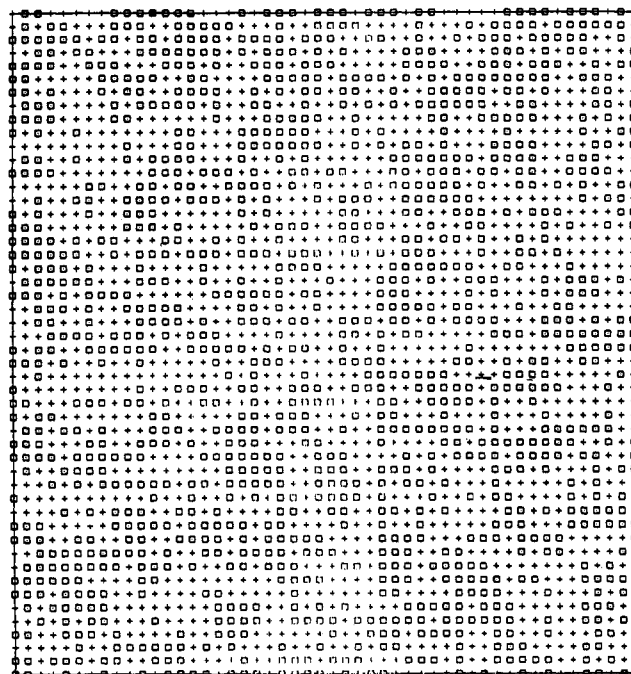


Figure 1. Monte Carlo simulation of the monomer–monomer model in $d = 2$ for $x = y = 0$ and $p = 10^{-3}$. The squares are A and the crosses, B (the lattice is full). (a, Top) Distribution of reactants at $t = 1$. (b, Bottom) Distribution of reactants for time $t = 10\,000$.

scale with scaling behavior

$$\Lambda \approx p^{d_s/2-1} \quad (7)$$

Thus in this model, though no particle diffusion takes place, the spectral dimension determines the behavior of the segregation length. We recall that in a random walk problem this exponent d_s controls the time development of the number of distinct sites visited by a random walker [see review in ref 23].

In the dissymmetric model, we have a phase diagram for the concentration of reactants for various x and y . We present results in 1d since, in this confined environment, the role of fluctuations is the largest. Figure 3 shows an example of this diagram for a given $y = -0.3$ and $p = 5 \times 10^{-2}$ in $d = 1$. We show the densities and the reaction rates as a function of x . We see around $x = 0$

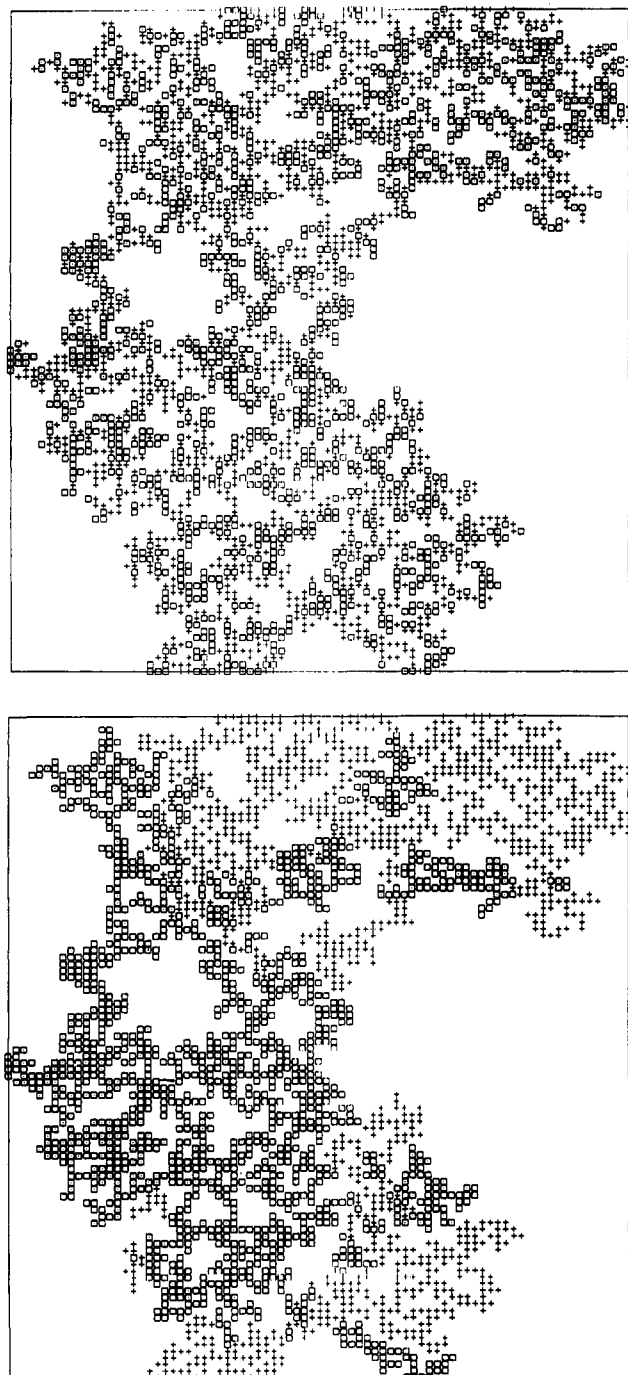


Figure 2. Monte Carlo simulation of the monomer-monomer model on the largest percolation cluster at criticality for $x = y = 0$ and $p = 10^{-4}$. The squares are the A species and the crosses the B species (the lattice is full). (a, Top) Distribution of reactants at $t = 1$. (b, Bottom) Distribution of reactants for time $t = 10\,000$.

a window of higher reaction rates with a typical width W_x . A classical picture would give a width $W_x = O(p)$ for a reaction rate $Q = O(1)$.²⁴

In Figure 4 we present results of Monte Carlo simulations. We plot the reaction rate rescaled by the segregation length, using the value of the spectral dimensions $d_s = 1$ (cf. eq 7) as a function of x multiplied by the segregation length). We see, for a set of different p parameters ($p = 5 \times 10^{-2}$, $p = 5 \times 10^{-3}$, $p = 5 \times 10^{-4}$), we have a reaction rate $Q = O(p^{1/2})$ for a window $W_x = O(p^{1/2})$. Thus we conclude that (i) the reaction window is larger than what is predicted by classical theory, and (ii) a self-organization takes place in this region since $Q = O(p^{1/2})$ and, according to eq 6, a mesoscopic length scale $\Lambda \approx p^{-1/2}$ shows up. The reaction rate depends on the geometry of the substrate.

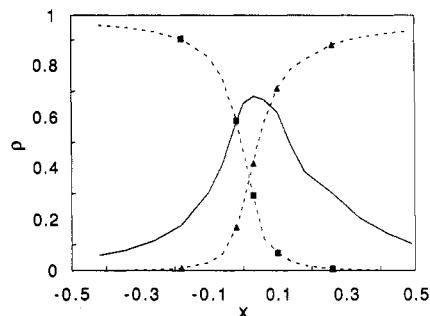


Figure 3. Phase diagrams for the species A and B as a function of x (adsorption dissymmetry) in $d = 1$. Here, $y = -0.3$, lattice size $L = 10\,000$, and $p = 5 \times 10^{-2}$. ρ_A is a solid line with squares, and ρ_B a dashed line with triangles. The solid line is 5 times the reaction rate/site: $5Q(x)$.

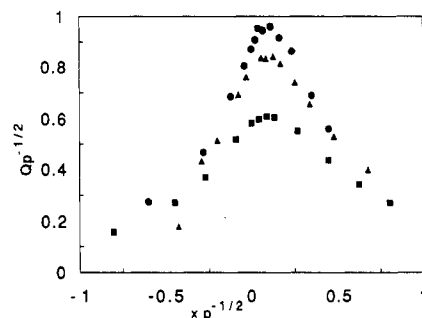
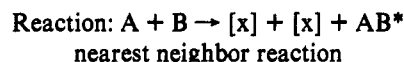
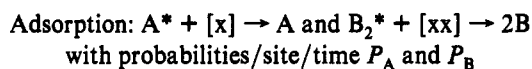


Figure 4. Rescaled reaction rate $Q(x) p^{-1/2}$ plotted as a function of $xp^{1/2}$ in $d = 1$; $y = -0.3$, lattice size $L = 10\,000$, and $p = 5 \times 10^{-2}$ (squares), $p = 5 \times 10^{-3}$ (triangles), $p = 5 \times 10^{-4}$ (circles).

A theoretical solution of this model explaining this behavior is in preparation using a mapping onto a spin model.²⁴ The persistence of the reaction anomaly associated with self-organization for $d_s < 2$ is demonstrated.

Monomer-Dimer Catalysis

Simple chemical reactions driven out of equilibrium can display a wealth of phenomena. One of the best studied is the monomer-dimer model for catalysis on a surface introduced by Ziff, Gulari, and Barshad.² It is a reasonable approximation to the oxidation of carbon monoxide on a platinum substrate. It consists of three steps:



Explicit diffusion of B can also be implemented. The control parameter of the reaction is $y = P_A/(P_A + 1/2P_B)$. A crucial point here is that B_2^* adsorption requires *two adjacent empty sites*, each of which captures one B atom, while A requires just one empty site. The original version of ZGB exhibits complex behavior with two phase transitions, a second-order transition between B poisoning and a reactive phase at $y = 0.389$ and a first-order transition between a reactive phase and an A-poisoned phases at $y = 0.525$. In the vicinity of the first-order transition, there are metastable states and the system shows hysteresis. Several variations of the ZGB model have been proposed and studied with diffusion of A, desorption, finite reaction rates, precursor adsorption, and species diffusion.²⁵ A mean-field theory of this process has been given by Dickman.²⁶

Recently, Goodman et al.²⁷ have shown that the trigger waves traveling from a stable state to a metastable state have a velocity depending on an *effective diffusion* constant: even when no explicit diffusion is present, a wave with a well-defined velocity occurs (in contradiction with classical results). This effective diffusion

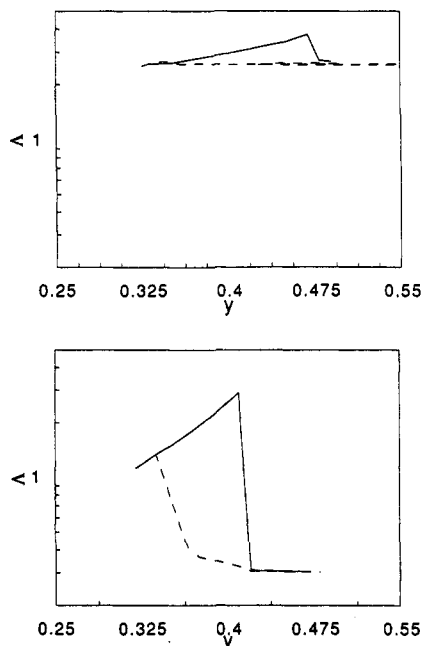


Figure 5. Segregation length Λ as a function of the adsorption dissymmetry parameter γ . The lattice size is 56×56 and the desorption of A, $P_A^d = 3 \times 10^{-4}$. The solid line is the steady-state value, starting with an empty lattice, and the dotted line is the steady-state value, starting with a lattice full of A. (a, Top) Fast diffusion ($\epsilon = 10$). (b, Bottom) Slow diffusion ($\epsilon = 0.1$).

seems to be related to the effective diffusion for monomer-monomer reactions. Also, the width of the waves is controlled by an unbounded (for infinite system) growth of the fluctuations given by a nonlinear KPZ equation.²⁸

In this paper, we are interested in reaction rate anomalies. We use a version of the ZGB model where explicit diffusion and desorption of A are implemented. The diffusion parameter is ϵ , which represents the probability/time of a jump of A in a nearest neighbor direction. The desorption probability/site of A is chosen to be $P_A^d = 3 \times 10^{-4}$. We monitor the reaction rate in the vicinity of the first-order phase transition. In Figure 5 we plot the self-organization scale Λ as a function of γ for two different initial conditions. The first (solid line) is for an empty lattice at initial time. The second (dotted line) is for a lattice initially filled with A. All the density and reaction rate values are measured in the steady state. Figure 5a shows Λ for a diffusion probability/time $\epsilon = 10$, and Figure 5b is the result for $\epsilon = 0.1$. Note that we have the transition location that depends on the values of P_A^d and ϵ . We clearly see the effect on the anomaly of the hysteretic behavior around the transition. The anomaly is the largest when the system is in the higher reactive metastable state. Moreover, we see also that the anomalous behavior is most expressed when the diffusion is slow (Figure 5b). Note that we also have found that the self-organization is the largest when no diffusion is present in the system, revealing, as in the study of the trigger waves, an effective diffusion term.²⁸ On the contrary, when the diffusion is fast, little organization takes place in the medium, and mean-field values for the reaction rates are almost correct.

Conclusion

In this paper we present results of Monte Carlo simulations of two elementary catalytic reaction models. We show that the internal fluctuations dominate. Fluctuations may create an effective diffusion term that modifies the reaction rate and produces self-organization in the system. This effect depends on the geometry of the substrate and modifies the curves of coexistence of the species in a way that no mean-field equation can predict. This anomalous effect is related to the anomalous behavior of diffusion-limited reactions which show nonclassical kinetics in low dimensions.^{17,18} The two models we study here are thus prototypes for deeper studies of the interaction among macroscopic behavior, nonlinear properties, and internal noise.

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