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LETTER TO THE EDITOR

Structure of the internal noise in a kinetic model of catalytic reaction

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Abstract

I study, by Monte Carlo simulations, the features of a model of catalytic reaction in which the dynamics of the slowest step of the reaction process is specified by a time random walk (TRW). This TRW aims at reproducing the actual dynamics of an adsorbed atom escaping out of a potential well.

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There has been sustained interest in a variety of kinetic reaction models which capture the major features of surface-catalysed reactions like the oxidation of carbon monoxide on platinum surfaces. Despite their simplicity, these models exhibit such interesting behaviour as bistability or irreversible phase transitions. They allow study of the complex dynamics of catalytic reactions, more specifically the study of the reaction noise or of the propagation of chemical waves between a stable phase and a less stable one. They pave the way to the elucidation of pattern formation. Reaction noise and patterns have been experimentally observed [1]. In addition, these models turn out to be simple enough to be solved, exactly or using some approximations; these solutions provide a deep insight into the dynamics of catalytic reactions. Finally, these models exhibit scaling properties which are of interest in their own right [2].

One of the simplest models in this field is the monomer–monomer model introduced by Fichthorn, Gulari and Ziff (FGZ) [3]. This model, studied by Monte Carlo simulations, was solved by Clément *et al* [4]. This model involves absorption and desorption of two monomers, A and B, on the sites of a lattice. When an A-occupied site is a nearest neighbour of a B-occupied site, A and B react and the emptied sites are randomly occupied either by A or by B:



where A and B are the monomers in the gaseous phase, A_{ad} and B_{ad} are the monomers adsorbed on a site of the surface and V denotes a vacant site of the surface. The FGZ model is symmetric: the absorption probability, $1/2$, and the desorption probability, p , are the same for both reactants so a unique parameter controls the reaction rate, which is p scaled by the length L of the lattice:

in one dimension, the scaled parameter [4] is $Lp^{1/2}$ and in two dimensions, $L^2p \ln(1/p)$. The FGZ model was generalized by Clément, Leroux-Hugon and Sander (CLS) [5] to the case of unequal absorption and desorption probabilities for A and B species. This generalized model has more flexibility. It displays bistability, like the FGZ model, and also an irreversible phase transition when only the reactant B is allowed to desorb. The CLS model was studied both analytically and by Monte Carlo simulations, and a good overall agreement found between the results from the two methods [5].

Studies of stochastic reaction models put the emphasis on the *spatial organization* of the reactants. For instance, the major feature of the FGZ model is the dramatic increase of the noise level when the (scaled) desorption probability p decreases: at low p , bursts of reactions are followed by nearly inert stages. This behaviour originates in the formation of mesoscopic patches of reactants of size Λ : $\Lambda \sim p^{1/2}$ in one dimension and $\Lambda \sim \ln(1/p)$ in two dimensions [4]. When $\Lambda \sim L$, the reaction is controlled by the stochastic evolution from a nearly A system to a nearly B system. Self-organization of reactants is also observed in more complex models like the monomer–dimer model introduced by Ziff *et al* [6] and many others [7]. By contrast, less attention has been paid to the *dynamics of the noise*, although this dynamics lies at the origin of the stochastic character of these reaction processes. In Monte Carlo simulations, a simple Markov process is used; i.e., desorption is accepted if a random number is lower than the probability p . In this letter, I address the question of whether the noise structure may influence the reaction process. Note that the noise in reaction models similar to the FGZ model may be termed *internal*, because it originates in the random organization of the reactants rather than from fluctuations of any of the parameters such as an absorption or a reaction rate.

A hint as to the importance of the structure of the noise in kinetic reaction models is given by the insightful papers of Wolf and Kertész [8]. These authors studied a very simple aggregation model—the Eden model—and showed that a *noise-reduction* procedure deeply affects the spatial organization at the boundary of the growing solid and accordingly the growth dynamics. In the original Eden model, aggregation of an atom hitting the perimeter of the solid is accepted with a probability p . In the noise-reduced model, a counter is attached to each perimeter site; a single hit on this site is accepted in the same probabilistic way as in the original model, but the aggregation of an atom is allowed only after m accepted hits, where $m > 1$. The noise reduction amounts to replacing the simple Markov process by a time random walk (TRW), a walk between the m states of the counter.

The TRW of [8] may be used for the desorption process of the CLS model; however, this procedure would lack physical justification. I propose instead a method which mimics the thermally driven escape over a potential barrier. I assume that the adsorbed atom, initially in its ground state, may be promoted to excited states. At each time step of a Monte Carlo process, the state of the atom performs either a move toward a higher excited state ($i \rightarrow i + 1$) with a probability δ , $\delta < 1/2$, or a move toward a lower excited state ($i \rightarrow i - 1$) with a probability $1 - \delta$. When entering the final state, the atom desorbs. Depending on the number m of internal states, δ is adjusted so as to yield, on average, the desorption probability p . The desorption dynamics is then controlled by a TRW between the m states of the adsorbed atom. Two features of this TRW are worthy of notice. In the first place, the second moment of the distribution of waiting time (WTD) is independent of m and equal to p^{-1} ; it may be proved that either the $m = 1$ process or $m > 1$ processes are Poissonian. Secondly, when plotting p versus δ in a log–log plot for various m , one gets straight lines; that is m plays the role of an *inverse temperature*, as surmised by Wolf and Kertész.

I will use this desorption dynamics in the CLS model, limiting myself to the fully asymmetric case: only the B reactant is allowed to desorb. In [5], one was left with only

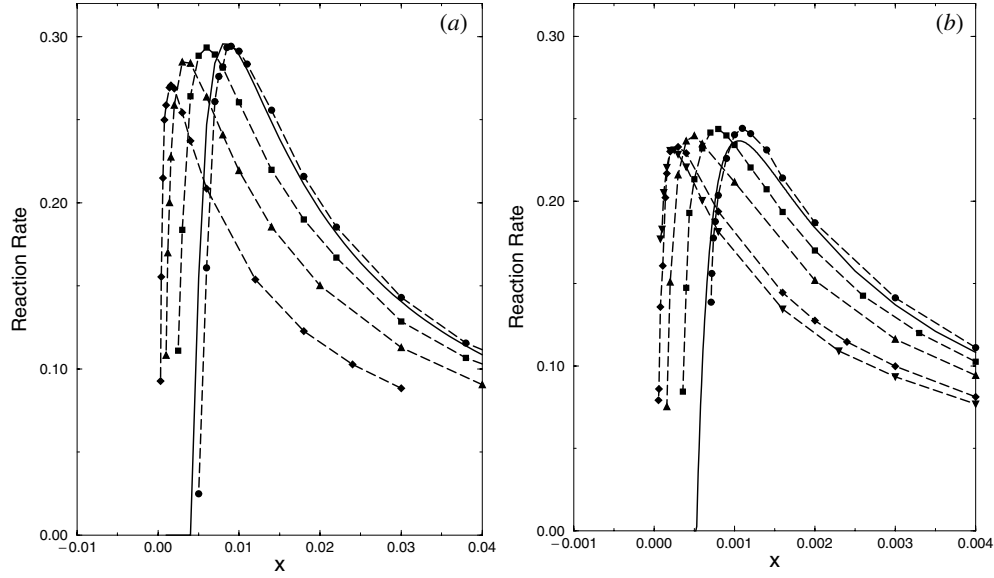


Figure 1. Reaction rate as a function of x in two dimensions. Solid curve: MF result; solid circles: Markov process; solid squares: TRW with two states; solid upward-pointing triangles: TRW with four states; solid diamonds: TRW with eight states; solid downward-pointing triangles: TRW with ten states. Dashed curves are guides for the eye. (a) $p = 0.01$, (b) $p = 0.001$.

two parameters: p and the ratio of adsorption probabilities

$$\frac{p_A^{(a)}}{p_B^{(a)}} = \frac{1-x}{1+x}$$

which defines the parameter x . For a given p , a reactive phase is present provided that x is larger than a critical value x_c , $x_c = x_c(p) > 0$. For $x \leq x_c$, all the lattice sites are A occupied and the reaction rate vanishes: this is an irreversible phase transition towards an absorbing phase.

I have studied, by Monte Carlo simulations, the way in which the dynamic phase transition of the CLS model is modified by the introduction of the TRW. I will concentrate on the curve giving the reaction rate R as a function of x , for two values of p . The generic curve shows a reaction window, specified by (i) the critical value x_c below which the system is in an absorbing phase, (ii) the value x_m of the maximum of R and (iii) the width of the reaction window, estimated as the width at half-maximum. In figures 1(a) and 1(b), R is plotted as a function of x for several values of the number of states of the TRW m ; note that $m = 1$, i.e. the original CLS model, obviously corresponds to a Markov process. Data are given for a square lattice, and for $p = 0.01$ and 0.001 . These low values of p assure us that desorption is the slowest process; reaction and adsorption are assumed to take place within the unit of time of the Monte Carlo trial. In these figures, I have also plotted results from mean-field (MF) theory [5]. As noticed in [5], Monte Carlo results for $m = 1$ are in agreement with the MF ones. As m increases, x_c and x_m decrease. This finding can be understood by considering the histogram of the WTD for different values of m . These distributions tend to be narrower and to have a maximum at longer time when m increases. For a plain desorption process, the average probability of desorption per unit time is independent of m (by construction, i.e. due to the choice of δ); however, in the presence of reaction the effective WTD has a cut-off, because the

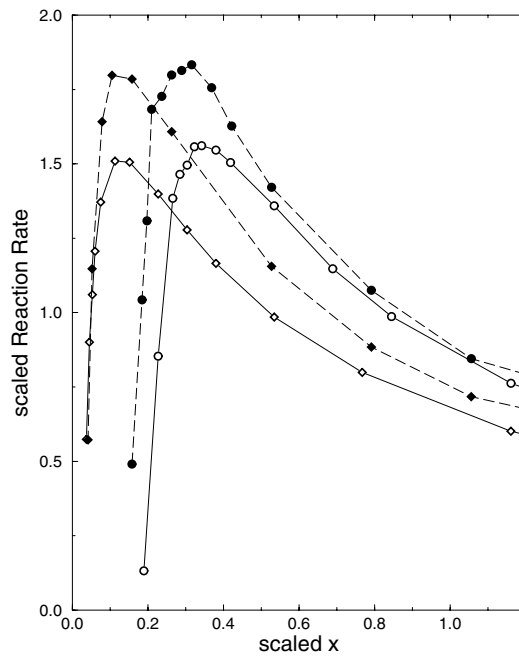


Figure 2. Scaled reaction rate R^* as a function of x^* in two dimensions. Solid circles: Markov process and $p = 0.01$; open circles: Markov process and $p = 0.001$. Solid diamonds: TRW with four states and $p = 0.01$; open diamonds: TRW with four states and $p = 0.001$. Curves are guides for the eye.

reaction opens a new channel for emptying a lattice site. The effect of this cut-off turns out to be more severe for m larger than 1. Also the width of the reaction window is lower for larger m . If one compares in figure 1(b) the $R(x)$ curves for $m = 1$ and 2, on the one hand, and those for $m = 8$ and 10, on the other hand, one notices that the variation of x_c with m in the former case is more important than in the latter case. That is, increasing m no longer has an effect beyond some limit. This feature is in agreement with the finding of Wolf and Kertész. A noticeable feature of the MF theory [5] is its scaling property: when x and R are plotted in scaled units ($R^* = R \ln(1/p)$ and $x^* = 2\pi x/p \ln(1/p)$), the critical values x_c^* , the values at the maximum of R^* , namely x_m^* , and the reaction widths tend to be the same. Interestingly, this feature is conserved for¹ $m > 1$, as displayed in figure 2 which shows the results for both values of p and for $m = 1$ and 4, plotted in scaled units, R^* as a function of x^* . In figures 3(a) and 3(b) similar results in one dimension are plotted, for $p = 0.01$ and 0.001 respectively. As noticed in [8], there is a significant difference between MF calculations and Monte Carlo results for $m = 1$: x_c and to a lesser extent x_m are larger in Monte Carlo results than in the theory. Presumably, the decoupling procedure does not properly account for the three-body space-correlation functions. Increasing m in the TRW tends also to lower x_c and x_m , but the difference is less important than in dimension 2.

Finally, I have checked that introducing the TRW does affect the spatial organization of the reactants, as expected [8]. Early studies of the FGZ model [3, 4, 9] have emphasized the

¹ Although this result is surprising—because for $m > 1$, the $R(x)$ curves depart from the MF ones—it is not fully unexpected. In the noise-reduced studies of [8], the spatial organization and the dynamics are deeply modified but the critical exponent stays unaltered.

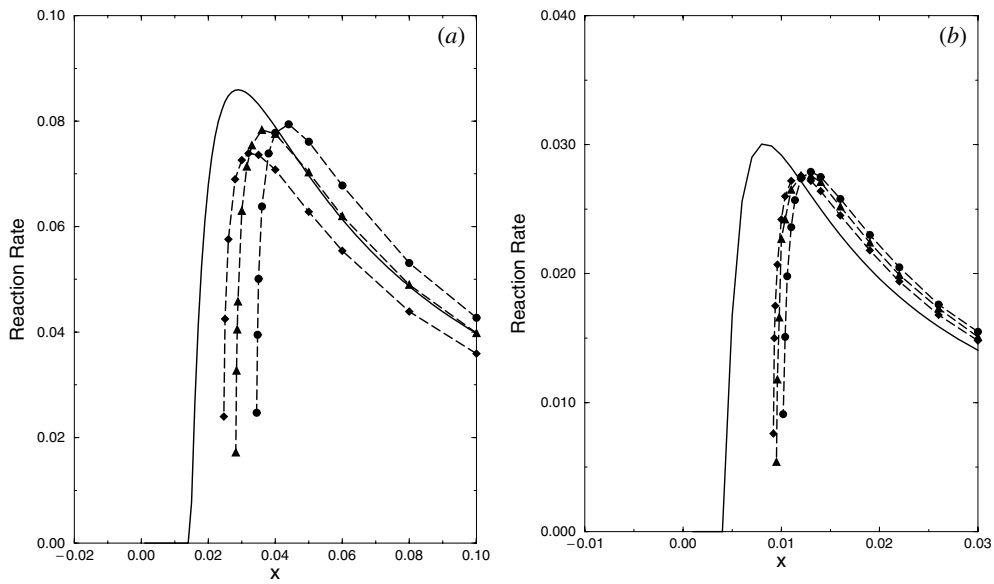


Figure 3. Reaction rate as a function of x in one dimension. The key is the same as for figure 1.

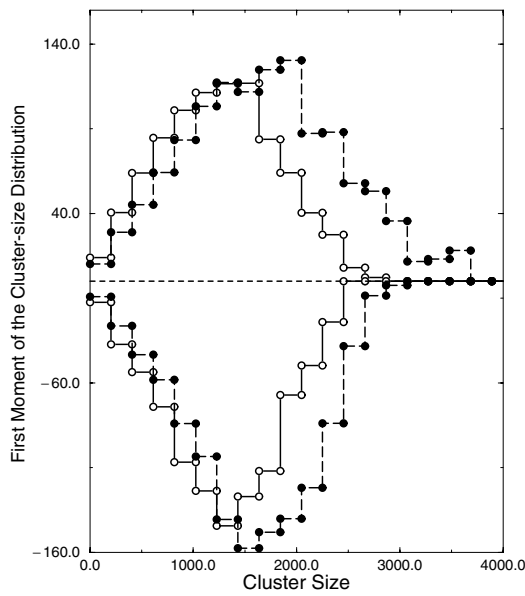


Figure 4. Histograms of the first moment of the cluster-size distributions as a function of cluster size for a 64×64 lattice, $p = 0.01$. Upper scale: A clusters; lower scale: B clusters. Solid line with open circles: Markov process; dashed line with solid circles: TRW with eight states. The A concentration is equal to the B concentration.

importance of the cluster-size distributions. In figure 3, I have plotted histograms of the first moment of the size distribution of the A and of the B clusters as a function of the size of the clusters, for $m = 1$ and 8 and for $p = 0.01$. In order to ensure that the comparison makes sense, I have chosen x such that the (average) A and B concentrations are equal; this is associated

with nearly the maximum of the $R(x)$ curves. The data correspond to averages over 2000 realizations. From this plot, we notice that (i) the A and B distributions are different and (ii) the TRW favours larger sizes for both A and B clusters.

To summarize, I have shown for a simple situation (transition towards an absorbing phase) that the introduction of a TRW which mimics the thermally activated desorption process significantly modifies the phase diagram of the CLS model, which is taken as generic. In addition, the fact that the number of states of the TRW plays the role of an inverse temperature is a step towards a more realistic description of a moderately complex reaction process. This suggests that the noise-reduction technique—a better term is noise-control technique—is not merely a computational trick to speed up the estimation of critical exponents, but may be endowed with a physical significance. Applications of this TRW concept to other features of the CLS model—e.g. the bistable situation, the cluster-size distribution, the output noise or the dynamics—are in progress.

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