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LETTER TO THE EDITOR

The monomer–dimer model of heterogeneous catalysis with a finite reaction rate

J Köhler and D ben-Avraham†

Interdisziplinäres Zentrum für Wissenschaftliches Rechnen (IWR), Universität Heidelberg, 6900 Heidelberg, Federal Republic of Germany

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Abstract. We study the Ziff–Gulari–Barshad monomer–dimer model for catalysis with finite reaction and adsorption rates. A recent paper shows numerical evidence for the existence of a tricritical point at a reaction probability value $r_c \approx 0.14$, below which there is no steady state reactive phase, but its *ad hoc* mean-field approach fails to reproduce this result. Our numerical simulations on significantly bigger lattices and using the more sensitive technique of *constant coverage*, show the absence of a tricritical point even for r as small as 0.01. We also conduct a mean-field analysis based on Dickman's cluster approximation, a self-contained method which does not require external parameters. It too supports our claim that there is no tricritical point in the monomer–dimer model with finite reaction rate.

In heterogeneous catalysis processes, reactants undergo a chemical reaction which is facilitated by their adsorption onto a catalytic surface. These systems have been traditionally studied using classical mean-field rate equations for the global concentrations of the reactants in question [1–3]. Lately, it has been realized that some important kinetic features arise from the fluctuations in the coverage concentrations of the catalytic surface in microscopic scales. These fluctuations may strongly interact and correlate with each other leading to collective kinetic behaviour which cannot be predicted by the classical approach. Lattice models which describe the process by a set of microscopic rules have dealt with the problem successfully.

The monomer–dimer lattice model for heterogeneous catalysis was introduced by Ziff, Gulari and Barshad (ZGB) to describe the oxidation of carbon monoxide on a platinum surface [4]. Their model consists of two elementary steps, namely reaction and adsorption, which take place with probability r or $s = 1 - r$, respectively. In an adsorption step, a deposition attempt is made either with a CO monomer (B) with probability p, or with an O_2 dimer (A_2) with probability $q = 1 - p$. The deposition attempt takes place at a randomly chosen lattice site on the surface. If the chosen site is empty and the impinging particle is a monomer, adsorption takes place. The adsorption of a dimer takes place only if in addition a randomly chosen nearest neighbour of the selected site is also empty. In a reaction step, neighbouring CO (B) and O (A) molecules bond to form carbon dioxide CO_2 (AB) which immediately desorbs from the lattice leaving behind two vacant sites. These steps can be symbolically represented by

$$B + * \rightarrow B* \tag{1a}$$

$$A_2 + 2* \rightarrow 2A* \tag{1b}$$

$$A* + B* \rightarrow AB + 2* \tag{1c}$$

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† Permanent address: Physics Department, Clarkson University, Potsdam, NY 13699, USA.

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where * denotes an active (empty) lattice site and A* and B* denote chemisorbed particles.

Let k_1, k_2 and k_r be the rates of the processes (1*a*), (1*b*) and (1*c*), respectively. In terms of these rates, *p*, *q* and the reaction probability *r* are given by $p = k_1/(k_1+k_2)$, $q = k_2/(k_1+k_2)$ and $r = k_r/(k_1+k_2+k_r)$. In the adsorption-limited case ($k_{1(2)}/k_r \rightarrow 0$, i.e. $r \rightarrow 1$) originally considered by ZGB [4], there is a reactive phase for $p_1 < p < p_2$, where the concentration of monomers, dimers and the production rate of AB is constant. For $p > p_2 (p < p_1)$ the lattice poisons with monomers (dimers).

In a recent paper [5] Considine, Takayasu and Redner (CTR) consider the ZGB model with a finite reaction rate. They first observe that in the reaction-limited case ($k_r/k_{1(2)} \rightarrow 0$, i.e. $r \rightarrow 0$) the kinetics of the process can be solved exactly, showing a direct transition from the monomer-poisoned to the dimer-poisoned phase at $p = 0.2$. There is no reactive steady state phase for $r = 0$. Their numerical simulations on a 32×32 square lattice suggest that at $r = r_c \approx 0.14 \pm 0.02$ there is a tricritical point; a reactive phase exists only for $r > r_c$. However, their mean-field analysis predicts a reactive phase which becomes narrower with decreasing *r* but which nevertheless persists down to $r = 0$.

In this letter we study the ZGB model with finite reaction rate in an attempt to resolve the question of the tricritical point. We extend the simulations of CTR to larger 300×300 lattices. The numerical search for a reactive phase at small values of *r* can be a tedious, time-consuming process. Fluctuations are typically large and even fairly big lattices poison because of their finite size. We tackle these problems by conducting simulations at a constant lattice coverage [6]. The mean-field analysis of CTR predicts no tricritical point, but it contains free parameters that are adjusted to fit the simulation data. We write down mean-field equations based on Dickman's cluster method [7] generalized for the case of finite *r*. While the final results are poorer than CTR, the method is systematic and self-contained, needing no external fitting of parameters, and in this sense it is complementary to the CTR approach. Both our simulations and mean-field results show no tricritical point at finite *r*.

For the actual simulation or process (1), the catalytic surface is modelled by a square lattice whose sites may be either empty (active) or occupied by point-like A or B particles. The description of the process given above can be literally taken as its simulation algorithm.

To speed up simulation, we keep a list of empty sites. Adsorption events are attempted only to sites in the list, thus avoiding trials that are sure to be rejected. After each adsorption attempt time is incremented by $1/N_E$, where N_E denotes the number of empty lattice sites. For the reaction step, we use a second list where we keep track of all AB-pairs. Choosing a pair of sites from this list, rather than from all possible pairs on the lattice, a reaction is guaranteed. This requires that we replace the reaction probability *r* by an effective probability

$$\tilde{r} = \frac{rN_{AB}/2}{rN_{AB}/2 + (1-r)N_E} \tag{2}$$

where N_{AB} denotes the number of AB pairs (notice that in an *N*-sites lattice there are $2N$ possible pairs). This is simply the ratio of the rate of successful reaction attempts to the total rate of successful event, reaction and adsorption, in the original process (without restricting attempts to sites on the special lists). After each reaction event the time counter is incremented by $2/N_{AB}$.

Using the simulation scheme above we reproduce the CTR results. For small reaction probabilities r, there appear to be no reactive phase and the lattice invariably poisons with either of the two species. The poisoning time near the transition from the monomer- to the dimer-poisoned phase increases algebraically with the size of the lattice N. The poisoning time near a reactive phase is known to grow exponentially with N [8], hence, one is tempted to conclude that there are no reactive states for small r and that a tricritical point must exist.

However, from the CTR simulation results as well as from ours, we observe that if a reactive phase existed at $r = 0.1$, say, its width would be expected to be $\Delta p \approx 0.001$. To resolve such fine details in the adsorption probability, a rate of adsorption events much larger than $1/\Delta p \approx 1000$ is required. But the number of adsorption events per unit time is $N_E = x_E N$, where x_E is the concentration of empty sites. One can estimate in our case, from the data near the first-order transition, that $x_E \approx 0.01$. Hence, a lattice much larger than $N = 1/(\Delta p x_E) \approx 10\,000$ is needed to resolve the differences in p. Our largest 300×300 lattices may not be large enough.

As an alternative to huge lattices we employ the *constant coverage* (CC) simulation algorithm which was introduced recently [6]. The CC algorithm keeps the coverage, that is the concentration of the reactants on the lattice, constant while allowing the adsorption rate p to vary. In this way, the resolution in p is independent of the lattice size.

Given the values for the reaction probability r and a target coverage of the lattice by monomers x_B^0, we first decide whether to execute a reaction (with probability $\tilde{r}$, equation (2)), or an adsorption event (with probability $1 - \tilde{r}$). Reaction events proceed as usual. The difference between the conventional simulation algorithm and CC is in the adsorption step. If $x_B < x_B^0$, an adsorption of a monomer B takes place, otherwise one attempts to adsorb an A_2 dimer. The number of B adsorptions and the total number of adsorption attempts is recorded and the monomer adsorption probability p is computed as their ratio. Because the convergence of p can be quite slow, a moving average provides with the best numerical estimate of p and of its error.

The CC algorithm was originally conceived to simulate the metastable states of the system near the first-order transition. Indeed, starting simulations with an empty lattice one can see the typical van der Waals loop of the metastable states. We have discovered that by starting simulations with a lattice half-full with monomers and half-empty, the system collapses to the first-order transition line. This is similar to the integration of dynamic mean-field rate equations. Also there the system evolves to the metastable states or to the first-order transition line depending on analogous initial conditions [6].

Our simulations were run on a Parsytec Supercluster, consisting of 128 T800 transputers with 4 Mbyte DRAM each. To obtain a phase diagram for a given reaction probability r, the CC algorithm was carried out simultaneously on several of the transputers, each with a different target coverage x_B^0. The simulations were run on a 300×300 lattice up to times $t \approx 10^7$. The CPU time required by each transputer depends on the concentration of empty sites (in one unit time there is an average of one adsorption attempt per empty site), it varied between 20 and 40 h.

In figure 1 we present results of the CC simulation for a reaction probability $r = 0.1$. Shown is the concentration of monomers x_B as a function of the monomer adsorption probability p. The loop of metastable and unstable states (indicated by the thin curve) is clearly resolved from the stable reactive states and the first-order transition (thick curve). The positions of the spinodal point S' and of the second-order trnsition point are hard to locate accurately. We estimate the probability at S' by fixing x_B^0 as close

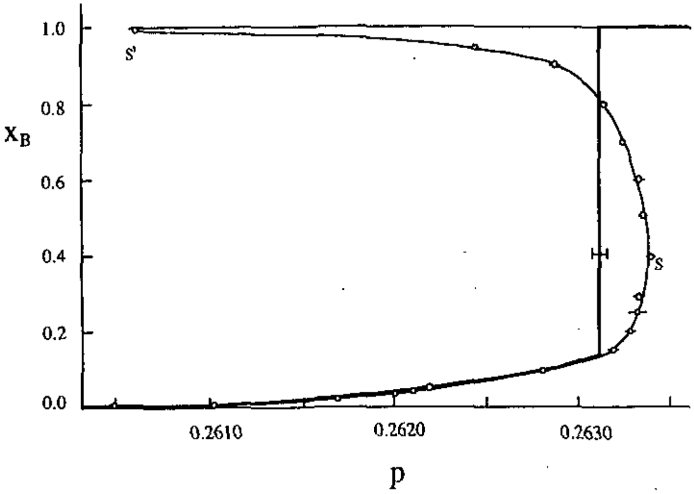

Figure 1. Steady state behaviour of the ZGB model at $r=0.1$. The open circles denote the CC simulation results, error bars are indicated whenever the error is larger than their diameter. The solid curves are drawn to guide the eye. The thick part denotes stable states and the thin part the loop of metastable and unstable states. The second-order transition point lies outside the range of the plot.

to 1 as possible. Likewise, the second-order transition probability is estimated by fixing x_B as close to 0 as possible.

Our data for $x_B=0.001$ indicate that the second-order transition at $r=0.1$ is at $p\approx 0.2527\pm 0.0002$. The first-order transition is at $p=0.26312\pm 0.00004$. Thus, the reactive region has a width $\Delta p\approx 0.01$. However, the concentration of empty sites is extremely low at a wide region around the second order transition point. It is a mere 0.003 at p as high as 0.261. Therefore, although Δp is relatively large, the product $x_E\Delta p$ is still small and enormous lattices would be required to see the reactive states with the conventional stimulation algorithm.

For smaller values of r, increasing amounts of time are required for the convergence of p and it is harder to obtain high quality data. Nevertheless, using the CC technique we were able to establish that there exists a reactive phase at $r=0.05$ with a width $\Delta p>0.002$ (the second-order transition estimate was obtained from $x_B=0.01$). We were also able to observe several reactive states at $r=0.01$ but made no attempt to establish the width of the reactive phase.

Following Dickman [7], we generalize his mean-field pair-approximation for the ZGB model to include finite reaction rates. The method is fully described in [7] and we use similar notation. In this technique, one writes down equations for the evolution of the concentration of all possible pair combinations. These concentrations we denote by x_{ij} where the indices i and j are A, B, or E, depending on whether we have an A or a B particle or an empty site, respectively. The concentrations add up to unity. $\Sigma_{ij}\, x_{ij}=1$, and the concentrations of j-sites is given by $x_j=\frac{1}{2}(x_{jj}+\Sigma_i\, x_{ij})$.

In the adsorption-limited case originally studied by Dickman there are seven different processes that one must consider. These processes consist of an adsorption, that may (or may not) be followed by *immediate* reaction events. The case of finite reaction rate is much simpler, because since reaction is no longer instantaneous, adsorption and reaction events are considered separately. We now have to keep track of only three different processes; the adsorption of a monomer (B↓), the adsorption of a dimer (A_2↓), and the reaction and desorption of a pair (AB↑).

Consider for example the process B↓. In the adsorption-limited case this is possible only if the B particle lands on an empty site which is not surrounded by A particles (otherwise an immediate reaction follows and the B particle is removed from the lattice). The rate of this process is $px_E(1-x_{EB}/2x_E)^4$. In the case of finite r, one does not need to worry about the neighbours of the vacancy. The adsorbed B particle remains on the lattice for a finite amount of time regardless of its neighbours and the rate is spx_E. Thus, also the rates of the different processes in the case of finite r are simpler than in the adsorption-limited case.

Whenever one of the three relevant processes takes place there is a change in the number of particle pairs ij, whose average, ΔN_{ij}, can be computed in terms of the various concentrations (see [7] for details). In this fashion, one obtains the pair-approximation mean-field equations

$$\frac{dx_{ij}}{dt}=\sum_k R^{(k)}\Delta N_{ij}^{(k)} \tag{3}$$

where $R^{(k)}$ is the rate of process k. The expressions for the rates and for $\Delta N_{ij}^{(k)}$ are presented in table 1. Notice that no column is included for AB pairs. The x_{AB} concentration is determined from $\Sigma_{ij}\, x_{ij}=1$.

Table 1. Rates and changes in pair numbers in the mean-field pair approximation.

Process	Rate	ΔN_{AA}	ΔN_{BB}	ΔN_{EE}	ΔN_{EA}	ΔN_{EB}
B↓	psx_E	0	$4\frac{x_{EB}}{2x_E}$	$-4\frac{x_{EE}}{x_E}$	$-4\frac{x_{EA}}{2x_E}$	$4\left(\frac{x_{EE}}{x_E}-\frac{x_{EB}}{2x_E}\right)$
A_2↓	qsx_{EE}	$1+6\frac{x_{EA}}{2x_E}$	0	$-1-6\frac{x_{EE}}{x_E}$	$6\left(\frac{x_{EE}}{x_E}-\frac{x_{EA}}{2x_E}\right)$	$-6\frac{x_{EB}}{2x_E}$
AB↑	rx_{AB}	$-3\frac{x_{AA}}{x_A}$	$-3\frac{x_{BB}}{x_B}$	$1+3\left(\frac{x_{EA}}{2x_A}+\frac{x_{EB}}{2x_B}\right)$	$3\left(\frac{x_{AA}}{x_A}+\frac{x_{AB}}{2x_B}-\frac{x_{EA}}{2x_A}\right)$	$3\left(\frac{x_{BB}}{x_B}+\frac{x_{AB}}{2x_B}-\frac{x_{EB}}{2x_B}\right)$

Our mean-field results are summarized in figures 2 and 3. In figure 2, we plot the phase diagram for $r=0.1$. Notice the strong similarity to the simulation results of figure 1. To plot figure 2, we have integrated equations (3) numerically. By starting with different initial conditions for the various pair concentrations the equations converge to the different branches of the phase diagram [7, 9]. However, we were not able to find a way to obtain the unstable branch of the loop SS'.

In figure 3 we plot the values of the probability p at the second- and first-order transition and at the spinodal point S as a function of r. There is a general agreement with simulation results and a reactive phase persists down to $r=0$.

Near $r=1$, there is good agreement with the results of Dickman [7]. For small r, the width of the reactive phase is largely exaggerated (it is 0.07 compared with 0.01 at $r=0.1$). Also, the transition point at $r=0$ differs from the exact value of $p=0.2$. The CTR mean-field predictions are much more satisfactory near $r=0$. The reason is that they base their approach on the number of *isolated* active sites. It is known that using this parameter the second-order transition can be mapped into its universality

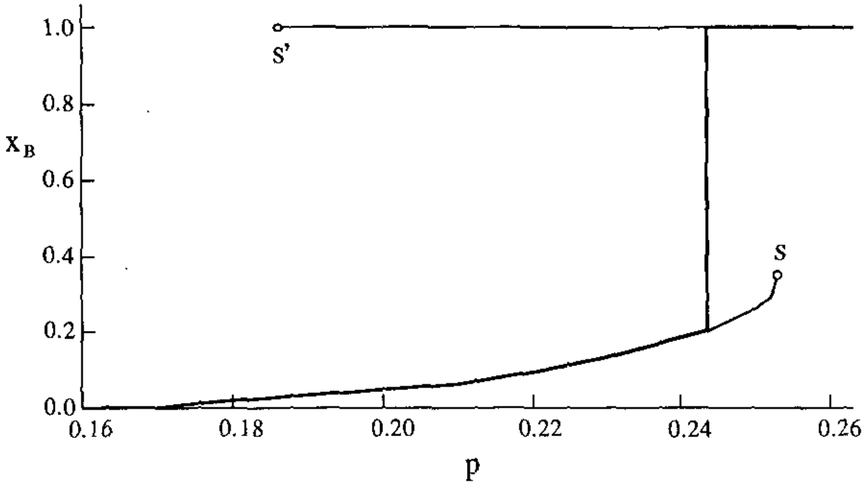

Figure 2. Steady state behaviour of the ZGB model at $r = 0.1$ as predicted from the mean-field pair approximations (3). The thick curve denotes the stable states and the thin one the metastable part of the loop. The unstable branch SS' cannot be obtained in our method.

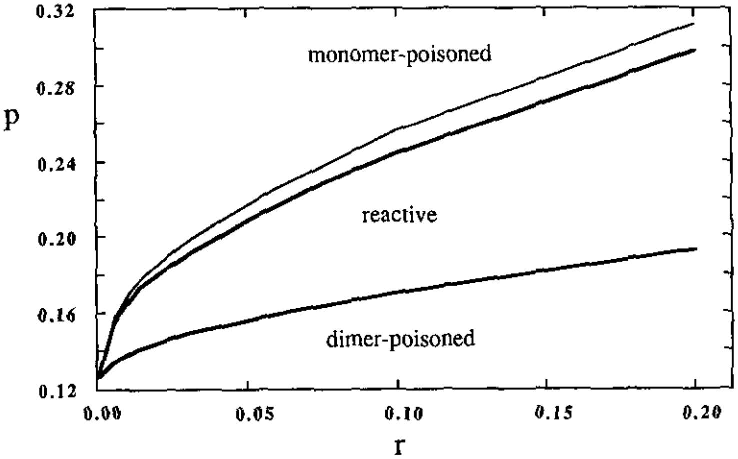

Figure 3. Phase diagram of the ZGB model for general reaction rates based on the mean-field pair approximation. The first-order (top) and second-order (bottom) transition lines are shown as thick curves. The spinodal line is denoted by the thin curve.

class of Reggeon field theory [10], while other coverage concentrations are irrelevant to this mapping. In our approach, the concentration of isolated empty sites is $x_e(1-x_{ee}/xe)^4$, which is only an approximation. On the other hand, our approximation has the merit of being self-contained and not resorting to externally adjusted parameters. In this sense, it is complementary to the CTR approach; together they make a strong mean-field argument against a tricritical point.

We have shown compelling evidence against the existence of a tricritical point in the ZGB model with finite reaction rates, both theoretical and numerical. Among our most important conclusions is the fact that on a finite lattice the adsorption probability cannot be resolved to arbitrary accuracy. The constant coverage simulation algorithm neatly overcomes this problem.

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