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LETTER TO THE EDITOR

A non-equilibrium tricritical point in the monomer-dimer catalysis model

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Abstract. We generalize the monomer-dimer model of heterogeneous catalysis, introduced by Ziff *et al* to allow for variable reaction and adsorption rates. Numerical simulations indicate that a steady state exists for a narrowing range of relative deposition rate of dimers to monomers as the reaction rate decreases. This steady-state regime disappears at a finite value of the reaction probability. A mean-field analysis suggests, however, that the steady-state regime extends to zero reaction probability.

In this letter, we give evidence for the existence of a non-equilibrium tricritical point in the monomer-dimer model of heterogeneous catalysis, when generalized to allow for variable reaction and adsorption rates. Much of the previous work [1-6] has considered the limiting case of slow adsorption and fast reaction—the adsorption-controlled limit. However, many catalytic processes occur in the opposite reaction-controlled limit [7], where the reaction on the surface is the limiting factor in the overall process. The possibility of varying the ratio between the reaction and adsorption rates gives rise to new kinetic phenomena and a richer phase diagram for the monomer-dimer model.

The monomer-dimer model was introduced by Ziff *et al* to describe the oxidation of carbon monoxide by a metal catalyst [1]. In their model, the catalysis involves two elemental sequential steps: adsorption and surface reaction. In the adsorption step, a deposition attempt is made by either an oxygen dimer (A_2), or a carbon monoxide monomer (B) with probability p or $q = 1 - p$ respectively. A deposition attempt of the chosen species takes place at a randomly selected site on the surface. If the site is already occupied, the deposition attempt fails. If the site is empty, adsorption can take place if the impinging particle is a monomer, thus creating an immobile surface-bound reactant B_s . However, if a dimer impinges on the surface, adsorption occurs only when a randomly chosen nearest-neighbour of the selected site is also empty. The adsorbed (immobile) dimer then dissociates into two atomic oxygens on the surface, which are denoted by A_s . In the reaction step, if a carbon monoxide and an oxygen atom are nearest neighbours on the surface, these two reactants bond to form a carbon dioxide molecule which desorbs immediately. This leaves behind two vacant sites which can then accommodate additional particles.

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These steps can be represented by the following reaction scheme:



where k_a and k_b are the adsorption rates of A's and B's, and k_r is the reaction rate of AB pairs [8]. In terms of these fundamental rates, $p = k_a/(k_a + k_b)$ and $q = k_b/(k_a + k_b)$, respectively, and the adsorption-limited model of Ziff *et al* corresponds to $k_a/k_r \rightarrow 0$ and $k_b/k_r \rightarrow 0$. An intriguing feature of this case is that for p in the range $0.475 \leq p \leq 0.611$, there is a reactive steady state, where the concentration of particles on the surface is constant and where there is a continuous production of AB molecules. Eventually, however, a finite-size system will saturate in a time which grows exponentially with the size [9]. For $p \rightarrow 0.611$ from below, there is a second-order kinetic transition to a state in which the surface is saturated with A's at long times, and there is no production of AB molecules. This transition has been shown to be in the same universality class as directed percolation and Reggeon field theory [2, 4, 6]. Similarly, when p decreases below 0.475, there is a first-order kinetic transition in which the surface is completely saturated with B's at long times, and AB production is again zero. For p outside the range 0.475–0.611, saturation takes place in a time which grows as a power of the system size or slower (see [8] for a study of the related monomer-monomer process in the adsorption- and reaction-controlled limits). Many aspects of these kinetic transitions can be accounted for within a mean-field approach [2–6].

When the ratio of adsorption to reaction rates is varied (the reaction-controlled limit of the monomer-dimer process was apparently first considered in [10]), a richer phase diagram is obtained in which the A and B saturated regimes are now separated from the steady-state regime by a line of second-order and first-order kinetic transitions, respectively (figure 1). As a function of p and of the reaction probability $r = k_r/(k_a + k_b + k_r)$, these two lines meet at a kinetic tricritical point which is located approximately at $p_c = 0.72 \pm 0.02$ and $r_c = 0.14 \pm 0.02$. The simulation for arbitrary adsorption and reaction rates is constructed by considering separating the two elemental steps that comprise the monomer-dimer process in the adsorption-controlled limit. First, a surface reaction or an adsorption is attempted with probability r and $1-r$, respectively. For the reaction step, a pair of nearest-neighbour sites is chosen at random and if the two sites are occupied by an AB pair, the two particles are removed. For the adsorption step, we employ the same algorithm used in previous simulations of the adsorption-limited model [1–3]. Our simulations were run on a single realization of a 32×32 square lattice. For a given value of r , a mesh of p values was examined with spacing 0.001 for $r \approx r_c$, and spacing 0.01 away from r_c . The steady-state regime was located when the mean saturation time (t), increased by an order of magnitude between successive mesh points, or if (t) exceeded 10^5 . For $r < r_c$, the saturation time reached a maximum value that was much less than 10^5 as p was varied, suggestive of a direct transition from the A-saturated to the B-saturated phase as a function of p .

Thus the simulations suggest that adsorption-controlled and the reaction-controlled limits of the monomer-dimer model exhibit drastically different behaviour. Within a mean-field context, it is easy to justify why this should be the case. In the adsorption-controlled limit, the probability of adsorbing a dimer is a quadratic function of the

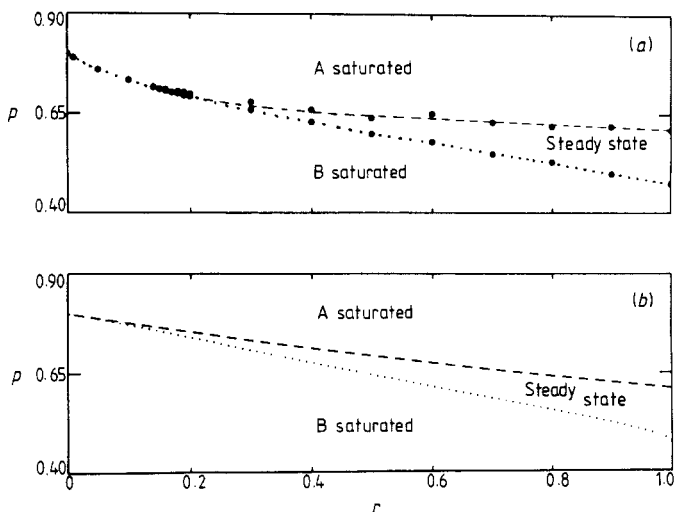


Figure 1. Phase diagram for the monomer-dimer model, for general adsorption and reaction rates based on (a) numerical simulations and (b) the generalized single-site mean-field theory discussed in the text. In (b), the values $c_1 \approx \frac{1}{8} + 0.19r$ and $c_2 \approx 0.24r$ were chosen. This *ad hoc* choice makes the transition points agree with the simulation results in the limit $r = 1$. The first- and second-order transition lines are shown dotted and broken, respectively.

fraction of empty sites on the surface, x_e , while the monomer adsorption probability is linear in x_e . Because of this difference, the relative probability of adding a dimer or a monomer depends on the surface concentration. Consequently, the rate equations which describe the evolution of the average densities of the two species can have a stable fixed point, corresponding to a steady state, for a particular non-zero range of the relative deposition rates. In the reaction-controlled limit, however, the surface is almost always full due to the slow surface reaction. Occasionally, a reaction occurs in which a single pair of vacant sites is created. This vacant two-site cluster can be filled only by a single dimer, or by a pair of monomers. The crucial point is that the relative probability of these two cases is *independent* of the concentration of reactants on the surface. Hence the corresponding rate equations contain no fixed points other than those corresponding to the saturated states, and there can be no steady state.

To provide a better qualitative understanding of the phase diagram, we present a mean-field analysis of the monomer-dimer model. Define x_i to be the concentration of species i , and x_{ij} to be concentration of nearest-neighbour ij pairs on the surface. Since adsorption of a dimer requires two vacant nearest-neighbour surface sites, the probability of a dimer deposition is proportional to x_{ee} , the concentration of pair vacancies. Similarly, the probability of a monomer deposition is proportional to x_e . Therefore the rate equations for the average concentration of A's and B's on the surface are,

$$\dot{x}_a = 2p(1+r)x_{ee} - rx_{ab} \quad (2a)$$

$$\dot{x}_b = (1-p)(1-r)x_e - rx_{ab}. \quad (2b)$$

A naive approximation for solving these equations would be assume a random distribution of reactants on the surface, so that $x_{ee} = x_e^2$ and $x_{ab} = x_a x_b$. The fixed-point analysis of the resulting rate equations is illustrated in figure 2(a). For k_a/k_b sufficiently

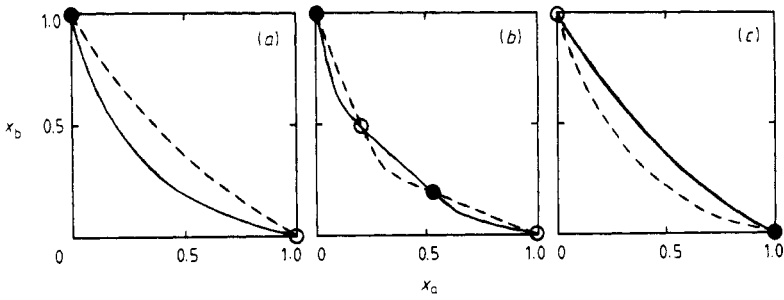


Figure 2. Schematic graph of the locus of points defined by $\dot{x}_a = 0$ (full) and $\dot{x}_b = 0$ (broken) in the rate equations (2), under the assumption $x_{ee} \propto x_c^2$. The intersection of these two loci defines either stable (\bullet) or unstable (\circ) fixed points. The locus $\dot{x}_a = 0$ approaches $(0, 1)$ and $(1, 0)$ with zero and infinite slope respectively, while the locus $\dot{x}_b = 0$ approaches these two points with finite slope. (a) The two fixed points that occur for small p . (b) The four fixed points that occur for larger p . From these fixed points, the phase diagram of (c) is obtained.

small, there are only two fixed points, with the stable one corresponding to the B-saturated phase. In the opposite case, there are four fixed points (two stable and two unstable), with an initially empty system being driven to the fixed point which corresponds to a steady state. These two possibilities yield the phase diagram of figure 2(b), which does not reproduce the simulation data.

The essential flaw in the above approach stems from neglecting the correlations between unoccupied sites, which arise because the A-B surface reaction creates nearest-neighbour *pairs* of vacancies. A conventional method to account for these correlations is to formulate a mean-field theory for the two-particle densities x_{ij} , in which higher-order correlation functions are factorized in terms of lower-order correlations. This 'pair' approximation [2] for the rate equations yields a satisfactory, but unwieldy, description of the monomer-dimer process in the adsorption-controlled limit. We therefore adopt an alternative and simpler approach which accounts for the strong pair correlations in the system within a single-site description. The basis of our approximation is that as $r \rightarrow 0$, the strongest correlations occur between empty sites, and this drives the essential asymmetry in the adsorption of A's and B's. We shall argue that this can be accounted for by writing x_{ee} in the power series form,

$$x_{ee} = c_1(p, r)x_c + c_2(p, r)x_c^2 + \dots \quad (3)$$

On the other hand, we claim that it is reasonable to factorize x_{ab} in (2b), since this quantity controls the reaction process which involves the A's and B's in a symmetric fashion.

To justify the power series expansion for x_{ee} , let us estimate the coefficients c_1 and c_2 . For small values of r , the surface is nearly filled by one species when the system is near the second-order A-B transition. Whenever an AB reaction occurs, an unoccupied pair is created and to a first approximation, these vacant pairs are isolated from each other. To lowest order in the reaction probability r , the vacancy can be filled either with 2 A's, by direct adsorption of a dimer, or with 2 B's, by sequential adsorption of two monomers. In the latter case, isolated vacancies appear as the intermediate step of the sequential filling process. By computing the rates at which the vacant pair can fill according to these two possibilities, we find that the average number of isolated sites, n_1 , equals $2n_2$, where n_2 is the number of vacant pairs. Consequently, for a square

lattice of V sites, the fraction of empty sites is $x_e = (n_1 + 2n_2)/2V = 4n_2/V$, while the fraction of empty bond pairs is $x_{ee} = n_2/V$. If one were to account for indirect filling processes, such as a monomer adsorbing onto vacant pair which reacts to form a vacant trimer before ultimate filling, one would find corrections to x_e and x_{ee} which involve higher powers of r . We thereby find $c_1(p, r \rightarrow 0) = \frac{1}{8} + rf(p, r)$, where $f(p, r)$ is non-singular in p and r . To find c_2 , we note that as $r \rightarrow 0$, vacancies are created *only* in pairs, and that these pairs are isolated. Consequently x_{ee} becomes a strictly linear function of x_e in this limit. This implies that c_2 must vanish as $r \rightarrow 0$, and the simplest assumption is to take $c_2(p, r \rightarrow 0) \propto r$.

By this approximation, we reduce the rate equations to a single-site description, from which a straightforward fixed point analysis (figure 3) yields the phase diagram. When the reaction and adsorption rates are systematically varied, there are three possibilities. For small p , there are only two fixed points, with the stable one corresponding to the B-saturated phase. As p increases, two new fixed points appear in a discontinuous fashion, corresponding to a sudden drop in the concentration of B's on the surface. This accounts for the first-order transition to the steady state. As p increases still further, two fixed points disappear in a continuous fashion, and the fixed point corresponding to the A-saturated phase becomes stable. This describes the second-order transition to the A-saturated phase.

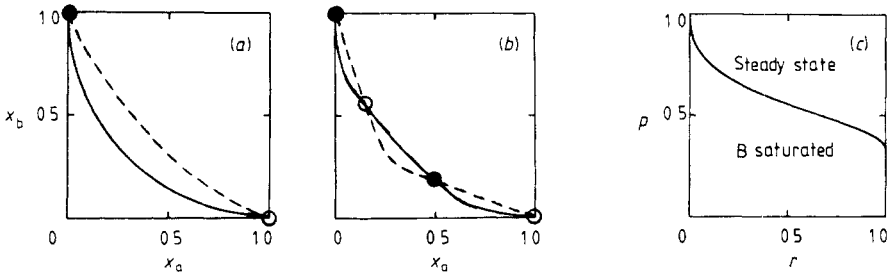


Figure 3. The fixed point structure of the rate equations (2), under the assumption $x_{ee} = c_1 x_e + c_2 x_e^2$. The evolution of the loci $\dot{x}_a = 0$ (full) and $\dot{x}_b = 0$ (broken) for increasing p is shown in (a)–(c). Both loci $\dot{x}_a = 0$ and $\dot{x}_b = 0$ approach (0, 1) and (1, 0) with finite slope. This leads to the occurrence of two fixed points (a), four fixed points (b), and again two fixed points (c). This leads to the phase diagram shown at the bottom of figure 1.

The resulting mean-field phase diagram (figure 1), qualitatively agrees with the simulations and is, in fact, superior to the pair approximation predictions. The presence of the first- and second-order transition lines and the three phases are reproduced. The primary discrepancy between the mean-field and the simulation is that in mean-field, a steady-state regime exists up to $r = 0$, while in the simulations the steady state disappears below a critical value of r . In mean-field theory, the width of the steady-state regime becomes vanishingly small as $r \rightarrow 0$, and it is difficult to resolve such a narrow region by simulation. For the system sizes that we considered, the available numerical evidence suggests that there is no steady-state regime for sufficiently small r . In particular, for a fixed system size, the mean saturation time initially decreases as one moves along the phase boundary away from $r = 0$. Furthermore, we have probed carefully the evolution of various initial states for a very fine mesh of p values for a single value $r = 0.1$, which is below our estimate of $r_c \approx 0.14$. We find that for all the initial conditions we attempted the transition between saturation to all A's and all B's

occurs at a single value of p . Taken together, these two tests suggest a tricritical point at a non-zero value of r_c . However, it is possible that a steady-state regime, too narrow to resolve with the small size system that we can simulate, exists down to $r=0$.

In summary, we have presented numerical simulations of the monomer-dimer model of catalysis for arbitrary adsorption and reaction rates. Numerical simulations indicate that a kinetic tricritical point at $r_c \approx 0.14 \pm 0.02$, $p_c \approx 0.72 \pm 0.02$ occurs, where the three phases of A-saturated, B-saturated, and steady state all meet. A simple modification of a conventional mean-field theory has been developed which provides a good qualitative description of the phase diagram.

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