Excluded volume effects in heterogeneous catalysis: reactions between 'dollars' and 'dimes'

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Abstract. We introduce a lattice model of catalysis which involves a small particle (a dime) and a large particle (a dollar). The larger diameter of the dollar prevents its adsorption next to a site which is already occupied by a dollar. The catalytic process is the reaction and immediate desorption of nearest-neighbour dime–dollar adsorbates. As a function of the reaction rate and the relative deposition rates of the two species, this system exhibits a second-order kinetic phase transition which separates a dime-saturated phase from a reactive steady state. The features of the phase transition are examined by numerical simulations and analytic techniques, including a systematic mean-field cluster expansion.

1. Introduction

There has been considerable effort recently devoted to the investigation of lattice models of catalysis [1–4]. One motivation for this effort is to construct models which capture some of the essential basic steps of catalytic reactions, while keeping them simple enough to investigate, either analytically or numerically. By these means, it is hoped to develop a better insight into the kinetics of real catalytic processes. One very important advance of this type was the introduction of the monomer–dimer model by Ziff, Gulari and Barshad (ZGB) to describe the oxidation of carbon monoxide on metal surfaces [1]. In this model, carbon monoxide adsorbs onto single vacant sites, while oxygen requires two adjacent vacant sites for dissociative adsorption. A nearest-neighbour pair of adsorbates, comprising an adsorbed carbon monoxide and an adsorbed oxygen atom, can bond to form carbon dioxide which then desorbs from the surface.

This monomer–dimer model exhibits non-equilibrium phase transitions, a feature which has generated considerable interest [1,5,6]. As a function of the relative adsorption probabilities of oxygen, p_O, and carbon monoxide, $p_{CO} = 1 - p_O$, there is a second-order transition from an oxygen-saturated phase to a reactive steady state when p_O decreases through 0.611. For $p_O > 0.611$, an initially empty system will eventually fill with adsorbed oxygen atoms and no further reaction is possible. At $p_O \simeq 0.475$, there is a first-order transition, below which an initially empty system fills with adsorbed carbon monoxide. Between these two transition points, both species, as well as vacant sites, are always present and a steady reaction process ensues.

The richness of the monomer–dimer model has spawned attempts to construct related lattice models and study the range of their non-equilibrium phase transition behaviour. One such example is the monomer–monomer model [3, 5], in which particles of two different species, A and B, adsorb onto single empty sites, with probabilities p_A and $p_B = 1 - p_A$, respectively. Adjacent A–B pairs react and desorb from the lattice. The lattice saturates with A's if $p_A > \frac{1}{2}$ and saturates with B's otherwise. At $p_A = \frac{1}{2}$, fluctuations play an essential role in governing the kinetics, and a finite-size lattice saturates with one of the two species quite slowly. In an infinite lattice, the point $p_A = \frac{1}{2}$ corresponds to a first-order transition from an A-saturated to a B-saturated phase. Another related example is the A model [2], a single-component system in which particles desorb at a constant rate but can adsorb only onto vacant sites which have at least one neighbouring adsorbed particle. This model exhibits a single second-order transition between an empty and a reactive steady state as a function of the adsorption and desorption rates.

The aforementioned examples illustrate how microscopic details, such as the number of sites required for the adsorption of a compound, play a crucial role in determining the behaviour of the system. This latter aspect motivates us to introduce a model for the catalytic reaction of 'dollars and dimes' (Dd model), where the adsorbates are no longer point particles, and their physical size is a determining factor in the process. The Dd model is stoichiometrically equivalent to the monomer–monomer model, $A + B \rightarrow AB \uparrow$. On the other hand, the geometrical restrictions imposed by the size of the particles render it similar to the monomer–dimer model. Nevertheless, the Dd model displays kinetic behaviour which is different from both the monomer–monomer and monomer–dimer models. This is further illustration of the essential changes in macroscopic dynamic phenomena brought about by slight changes in microscopic details.

Another motivation for our work is that general arguments have recently been given by Grinstein *et al* which suggest that the second-order transition of the monomer–dimer model and, in fact, of a broad class of surface catalysis models with a unique absorbing state, is in the same universality class as Reggeon field theory [7]. (One notable counter-example is the dimer–trimer model which exhibits a phase diagram similar to the ZGB model [8], but with a second-order transition that appears to belong to a different universality class.) The Dd model is another testing ground which appears to confirm this universality hypothesis. Additionally, the Dd model is amenable to a variety of mean-field cluster expansions [6, 9]. These represent a systematic improvement of classical mean-field theory, in which the exact configurational information within a cluster of a given size is retained, while higher-order correlations are truncated as the product of lower-order correlations. These systematic methods turn out to be relatively difficult to apply for both the monomer–monomer and monomer–dimer models. Thus the Dd model also serves as a useful testing ground for the development of these systematic techniques.

2. The model

The dollars and dimes model can be viewed as a simple variant of the monomer–monomer process in which one of the two species, (the D's, for example) have a diameter which is larger than a lattice spacing. Consequently, D's can adsorb only onto empty sites which have no D nearest neighbours, so that nearest-neighbour pairs of adsorbed D's cannot exist. The diameter of the d particles is smaller than a lattice spacing and they can adsorb onto any empty site, regardless of the occupancy of its neighbours. One can picture the d's as dimes
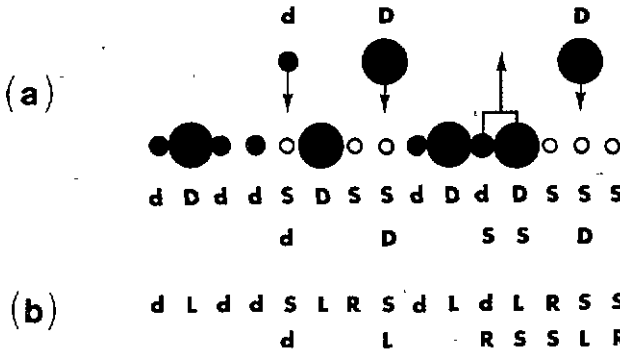
Figure 1. The dollars and dimes model represented as a reaction of (a) large particles D and smaller particles d, and (b) as a reaction of d particles with directed LR dimers. The changes in the states of each site as a result of various processes are indicated in the lower row of characters, in both representations.

and the D's as larger dollar coins, which provides a simple visualization of the excluded volume constraint in the model (figure 1(a)).

According to these conditions, the reaction consists of the following kinetic steps:

$$D + S' \xrightarrow{k_D} D_s$$

$$d + S \xrightarrow{k_d} d_s \tag{1}$$

$$D_s + d_s \xrightarrow{k_r} Dd \uparrow + S + S'.$$

Here the subscript s denotes adsorbed particles, S denotes a vacant lattice site, and a prime indicates the further restriction of a vacant site with none of its neighbours occupied by a D. Since the D particle of the D_s–d_s pair in the last step of the process does not have D nearest neighbours, one of the sites freed upon desorption must be S', thus ensuring the catalytic nature of the process (the lattice sites S and S' remain unchanged through a cycle). The net effect of process (1) is the conversion $D + d \to Dd \uparrow$, just as in the monomer–monomer model. However, we shall see that the special requirements for the adsorption of D's gives rise to different kinetics.

An interesting aspect of the the Dd model in one dimension is that it can be mapped onto a variant of the monomer–dimer model in which the dimer has a directionality. This equivalence is achieved by the replacements

$$DS \leftrightarrow LR \qquad Dd \leftrightarrow Ld$$

(figure 1(b)). Here DS denotes a pair of sites, in which the left site is occupied by a dollar and the right site is vacant, and LR denotes the equivalent dimer, with a well defined 'tail' at the left (L) and a 'head' to the right (R). Thus a dollar and only an adjacent vacant site to its right are replaced by a directed dimer LR. Dimes can adsorb on either the vacant sites or on the head of a directed dimer (which is also a vacant site). Thus we have a directed monomer–dimer model, with some degree of multiple occupancy allowed. The fact that the Dd model kinetics is so different from the ZGB monomer–dimer model is another demonstration of the importance of microscopic details.

3. Simulation results

Simulations of the Dd model were performed for general values of the rates in equation (1). For a surface which contains N_D D's, N_d d's, N_S vacant sites, and N_{Dd} nearest-neighbour Dd pairs, the total rate for a single event to occur (either adsorption *attempt* or surface reaction) is $\mathcal{R} = (k_D + k_d)N_S + k_r N_{Dd}$. Thus the probability for the occurrence of an adsorption attempt being $p_{ads} = (k_D + k_d)N_S/\mathcal{R}$, and the probability for the occurrence of a reaction event is $p_{reac} = 1 - p_{ads}$.
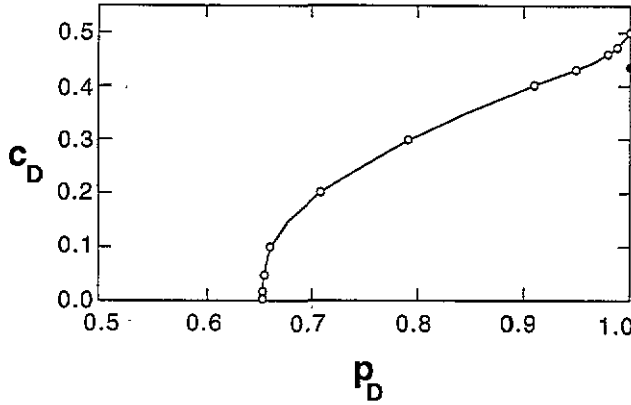

Figure 2. Simulation results for the Dd model in one dimension in the adsorption-limited case. The long-time limiting concentration of dollars (D) as a function of their adsorption rate p_D is shown. Notice the discontinuous transition to the dollar-jammed phase at $p_D = 1$, indicated by a full circle.

In each microscopic event, adsorption is chosen with probability p_{ads} and a reaction event is chosen otherwise. For the former process, adsorption of a D or a d is attempted onto an empty substrate site, with respective probabilities $p_D = k_D/(k_D + k_d)$ and $p_d = 1 - p_D$. If a D is selected to occupy a given vacant site, then we additionally check whether any of the nearest neighbours of the selected site are occupied by a D. If this is the case, then the adsorption attempt fails, and this completes one elementary step. A reaction occurs by having one nearest-neighbour Dd pair desorb. After these elemental steps are completed, the time is incremented by $1/\mathcal{R}$ and the number of the various species and the number of Dd bonds is updated. The repeated application of this sequence of events yields a simple algorithm for the kinetics when the microscopic rates have arbitrary values.

For the adsorption-controlled limit, $(k_D + k_d)/k_r \to 0$, reactions occur immediately following adsorption events, whenever possible. In the complementary reaction-controlled limit, $(k_D + k_d)/k_r \to \infty$, the lattice is always full and after each reaction event adsorption is immediately performed onto the freed lattice sites. To simulate these two limiting cases requires only straightforward modifications of the general algorithm.

A plot of the steady-state concentration of D's, c_D, as a function of the adsorption probability, p_D, is shown in figure 2 for the adsorption-limited case. One observes a dime-saturated phase, and a reactive steady state. The transition between these two phases is second order and occurs at $p_D \approx 0.653$ in the adsorption-limited case. In addition to this phase transition, there is a discontinuity at $p_D = 1$. When $p_D = 1$, the Dd model reduces to

the random sequential adsorption of dimers [10], where the lattice saturates with a mixture of dollars and vacant sites, with $c_D = (1 - e^{-2})/2 \simeq 0.4323$. On the other hand, an infinitesimal adsorption probability for the dimes is sufficient to sustain a reactive stationary state. The adsorption and subsequent reaction of the dimes helps redistribute the vacant sites in the lattice. In this way, a more efficient packing of dollars can be sustained. When $p_D \to 1^-$, the system eventually relaxes to the tightest packing possible, of alternating D's and S's, and $c_D = 0.5$.

For general reaction rate, the transition between the dime-saturated and the reactive phase shifts to higher values of p_D as p_{reac} decreases. At $p_{reac} = 0$ the lattice saturates with dimes for all p_D. This follows because the two sites freed during a reaction event are refilled immediately, and this can be accomplished only by two dimes or by a dime–dollar pair. Hence, the concentration of dollars can never increase, leading to an eventual saturation with dimes. The phase diagram for general adsorption and reaction probabilities is shown in figure 3. Our numerical simulations suggest that the slope of the transition line between the saturated and reactive phases at the point $(p_{reac}, p_D) = (0, 1)$ is infinite. This is also supported by a mean-field cluster approximation (details of that approximation are given below). In higher dimensions, the phase diagram exhibits the same qualitative features as in one dimension.
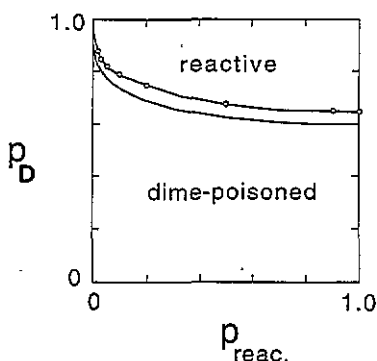

Figure 3. Phase diagram of the Dd model for general adsorption and reaction rates in one dimension. The transition line between the reactive and saturated phases is drawn in the p_D–p_{reac} plane. The open circles represent simulation data, while the lower curve is derived from a three-site mean-field cluster approximation.

4. Phase diagrams and transition points

As discussed above, the Dd model is stoichiometrically equivalent to the monomer–monomer model, and it also shares some microscopic similarities with both the monomer–monomer model and the ZGB monomer–dimer model. Nevertheless, the macroscopic behaviour arising from the slight changes between the three models is quite different. In figure 4, we schematically compare the long-time asymptotic behaviour of these three systems. The respective phase diagrams are arranged so that equivalent transition points are positioned directly below each other. A correspondence is made between the monomers and dimers of the ZGB model, and the dimes and dollars of the Dd model, respectively. In
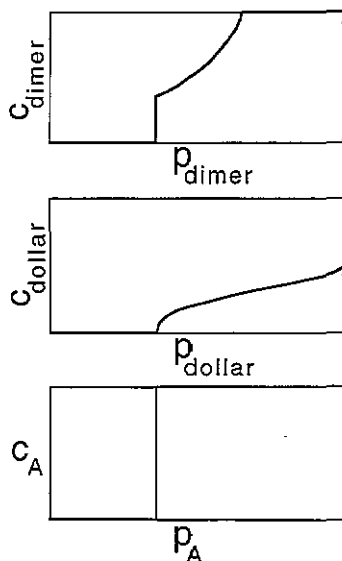
Figure 4. Schematic phase diagrams for the ZGB model (in greater the one dimension), the Dd model, and the monomer–monomer model (top to bottom). The concentrations of reactants as a function of their respective adsorption probabilities are shown. Analogous transition points are positioned directly below each other.

the monomer–monomer model, the roles played by the two species is symmetric. Therefore we have arbitrarily chosen the A's to be compared to the dollars and the B's to the dimes.

The dime-saturated phase of the Dd model is exactly analogous to the monomer-saturated phase in the ZGB model, and to the B-saturated phase in the monomer–monomer model. However, the remainder of the phase diagram is different for the three systems. In the monomer–monomer model there is a sharp transition to an A-saturated phase. The ZGB and Dd models instead exhibit a transition to a reactive steady state, but the transition is first order in the ZGB model and second order in the Dd model. In the ZGB model there is an additional second-order transition to a dimer-saturated phase, a feature which has no analogue in the Dd model. Indeed, saturation with dollars is not possible in the Dd model, for as long as there is a finite probability of adsorption of dimes, the dimes can land in the interstices between dollars and maintain a reactive steady state. Finally, jamming with dimers or dollars is observed when the adsorption rates for monomers or dimes is zero. The transition to this jammed state is discontinuous, but it happens from a reactive state in the Dd model and from a dimer-saturated phase in the ZGB model.

The phase diagram of the Dd model is different from that of the monomer–monomer or the ZGB model, but does resemble that of the A model mentioned in the introduction. For the A model, the second-order transition between the empty state and the reactive state was shown to belong to the same universality class as Reggeon field theory (RFT), a universality class which also includes directed percolation and the second-order transition between the reactive state and the dimer-saturated phase of the ZGB model. It is therefore natural to inquire whether the phase transition in the Dd model is also in the RFT class. Grinstein *et al* [7] have given a general argument that any second-order kinetic phase transition from a single absorbing state to a reactive steady state should belong to the RFT class. The transition point of the Dd model should be no exception to this rule. Indeed, our numerical simulations results in one dimension are roughly consistent with an RFT-type of transition.

This is further confirmed by the mean-field cluster analysis discussed in the next section.

We find it intriguing that the transition point of the Dd model is in the RFT universality class while the analogous transition points in the ZGB model and in the monomer–monomer model are not even second order (cf figure 4). According to the argument of Grinstein *et al*, near the transition to a saturated phase there is a progressively smaller concentration of single empty sites, pairs of empty sites, triplets of empty sites, etc. Therefore, it is justifiable to treat the smallest clusters, of one and two empty sites exactly, and approximate the concentration of larger clusters in a mean-field spirit. Following this approach one can write down a set of coupled reaction–diffusion equations for the concentrations of one- and two-sites clusters of empty sites. Upon diagonalizing these equations, one of the (orthogonal) fields has a negative eigenvalue which means that it can be renormalized away. The other field is associated with an eigenvalue that changes sign at a critical value of the rate parameters. This, and the fact that the latter field satisfies a RFT diffusion–reaction equation, suggests that the system undergoes a RFT transition.

The argument of Grinstein *et al* also predicts that the transition of the Dd model belongs to the RFT universality class. However, their criterion is not conclusive. For example, it also predicts that the one-dimensional ZGB model is in the RFT universality class, even though simulation clearly shows that the second-order transition does not exist. Thus the Grinstein *et al* argument provides an indication that the Dd model is in the RFT universality class, but the criterion cannot be regarded as definitive.

5. Mean-field cluster approximation

Another analytical method for analysing the kinetics of the Dd model is a systematic cluster approximation in which one writes rate equations for the evolution of the probability of having a cluster of size n in a specified state. The time development of an n-site cluster is generally influenced by the state of even larger clusters which contain the initial n-site cluster. Thus, there results an infinite hierarchy of rate equations which usually cannot be solved exactly. Mean-field techniques consist of cutting off this hierarchy by approximating the probabilities of clusters beyond a certain size in terms of products of state probabilities of clusters which are smaller than the cutoff [6, 9]

Mean-field approximations are expected, at the very least, to predict the correct qualitative features of phase diagrams. With an increase in the approximation degree (i.e. the cutoff size of the cluster), one expects kinetic predictions to become progressively more accurate on a quantitative level as well. So far, mean-field techniques have been employed mostly in the former sense, as a predictor of the general features of phase diagrams. Recently, the potential of the mean-field cluster approximation for the study of quantitative features has been explored [9]. For models in dimensions greater than one, we have not yet been able to find a systematic and tractable way to improve the approximation degree. The essential difficulty is in devising a consistent strategy for the truncation of large clusters in terms of groups of smaller clusters. In one dimension, however, an approximation method has been developed which does allow one to increase the cluster size systematically [9]. Unfortunately, the phase transition behaviour disappears in one dimension for many lattice models. However, the Dd model and the single-component A model do exhibit a kinetic phase transition in one dimension. Thus, these two models serve as a useful test of our systematic cluster mean-field techniques.

The mean-field predictions yield, as expected, the correct qualitative features of the phase diagram of the Dd model for general rates, even in one dimension (see figure 3). In

figure 5, we plot c_D against p_D based on the mean-field cluster approximation for increasing cluster size in the adsorption-limited case. It is evident from the figure that the mean-field data converge to the simulation results. Curves for up to the four-site approximation are shown, and we have obtained results for up to eight-site clusters.
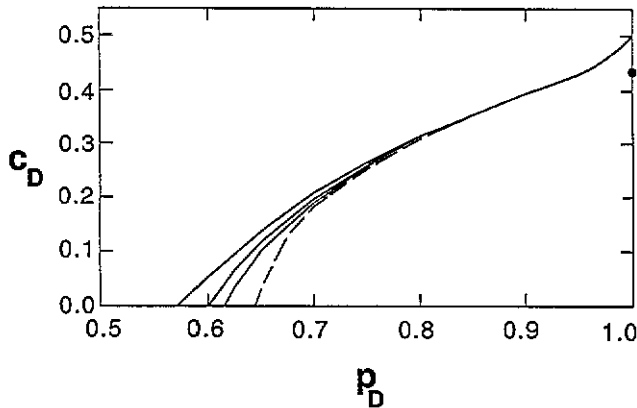

Figure 5. The cluster mean-field approximation for the one-dimensional Dd model in the adsorption-limited case. The concentration of dollars c_D against their adsorption probability p_D is shown. The curves from left to right represent the predictions from $n = 2, 3, 4$ in the n-site approximation, and the computer simulation results (broken curve).

The values of the critical adsorption probability obtained by the cluster approximation extrapolate to 0.6529 ± 0.0008, very close to our best numerical estimate of $p_c = 0.653$. The order parameter critical exponent, β, can be evaluated from the slope of the curves of c_D against p_D as they intersect the p_D-axis, by means of the coherent anomaly method [11]. Based on results for two successive cluster sizes of up to eight sites, we estimate $\beta = 0.29 \pm 0.05$ for the concentration of dollars, and $\beta = 0.27 \pm 0.05$ for the concentration of vacancies. These show a reasonable convergence to the best estimate of the β exponent for RFT in one dimension, of $\beta \simeq 0.277$.

6. Summary and discussion

We have presented the dollars and dimes model for heterogeneous catalysis, where the physical size of the adsorbed particles plays a significant role. While the Dd model is stoichiometrically equivalent to the monomer–monomer model, and also closely related to the ZGB model, its phase diagram and kinetic behaviour are different from either of these two cases, showing the importance of microscopic details. Indeed, the Dd model differs from the monomer–dimer model not only in its phase diagram, but also in some deeper characteristics such as the role of the spatial dimension: the monomer–dimer model exhibits different behaviour in dimensions $d = 1$ and 2, while the Dd model exhibits similar kinetics in all dimensions $d \geq 1$.

On the other hand, we have found that the second-order transition from a dime-poisoned phase to a reactive phase in the Dd model belongs to the RFT universality class. This supports the argument of Grinstein *et al* [7] that all second-order transitions from a single

absorbing state in dynamic lattice models are in the RFT universality class. We have tested this possibility both numerically and using a mean-field cluster approximation technique.

The Dd model sharpens the question of classification of dynamic lattice models. In view of the vast effects of microscopic details, it becomes apparent that some powerful criteria will be needed before one can foretell the behaviour of an arbitrary model. The argument in Grinstein *et al* [7] is a first step in that direction, in that it groups seemingly disparate models under the same universality class.

Among the many problems motivated by the Dd model one is the subject of current interest. Suppose one starts with a lattice jammed with dollars and then turns on a very small probability, ϵ, for adsorption of dimes (and a probability $1 - \epsilon$ for adsorption of dollars). The system will evolve to a new stationary state with a small steady reaction rate, proportional to ϵ, where the concentration of dollars achieves its possible maximum of $\frac{1}{2}$. That is, the minute adsorption of dimes acts as an annealing field that lets the system relax from the frozen disorder of jamming with dollars to a highly ordered, periodic state. A similar situation occurs in the ZGB monomer–dimer model if one turns on an ϵ adsorption rate of monomers, starting from a lattice initially jammed with dimers (only that here the system will eventually poison with dimers and reaction will stop). In a recent work, Privman and Nielaba [12] study a similar process where the dimers are allowed to diffuse in order to anneal. It would be interesting to see whether the relaxation kinetics in all these cases is essentially similar.

Acknowledgments

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