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LETTER TO THE EDITOR

The dimer–trimer model for heterogeneous catalysis: a new universality class

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Abstract. We study a new model for heterogeneous catalysis in which dimers A_2 and trimers B_3 are chemisorbed onto a triangular lattice. Nearest adsorbed A and B neighbours react and desorb, leaving behind two empty sites. We observe a phase diagram similar to that of the monomer–dimer model of Ziff, Gulari and Barshad with a stationary reactive phase in between a dimer-poisoned and a trimer-poisoned phase. There is a first-order transition from the reactive phase to the dimer-poisoned phase, and a second-order transition to the trimer-poisoned phase. However, the second-order transition is in a different universality class from Reggeon field theory, in contrast to all previously studied models for catalysis. The difference stems from the infinite number of absorbing states in the trimer-poisoned phase special to our model.

Heterogeneous catalysis is a process in which chemical reactants are adsorbed onto the surface in between two different phases and then undergo chemical reaction. The reaction rate is enhanced by the weakening of internal bonds in the chemisorbed molecules and by their physical proximity on the surface [1–3]. The process is of much practical importance because of its common use in chemical industry and in controlling toxic emissions into the environment. Traditionally, heterogeneous catalysis has been analysed by mean-field methods, using classical rate equations [1–3]. Recently, it has been realized that the absence of strong homogenizing mechanisms deem these methods ineffective and lattice models have been introduced to deal with the effects of microscopic fluctuations and correlations in the concentrations of the reactants [4–6]. Indeed, lattice models have succeeded in explaining a wide range of kinetic behaviour which was unaccounted for in the classical approach.

Perhaps, the simplest lattice model is the *monomer–monomer* model for the symbolic reaction $A + B \rightarrow AB$ [4–7]. The catalyst surface is modelled by a lattice of sites which are either empty (active), or occupied (inactive). At each time step, there is an attempted adsorption of either an A or a B particle with probabilities p and $1 - p$, respectively, to a randomly chosen lattice site. The particle is adsorbed if the site is active and rejected otherwise. Following an adsorption event, nearest-neighbour A–B pairs react and the product desorbs, freeing two sites that become reactivated. For $p > \frac{1}{2}$, the lattice eventually saturates with A particles and the process stops. If $p < \frac{1}{2}$ the lattice saturates with B particles. For the special case of $p = \frac{1}{2}$, if the lattice is

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infinite the process arrives at a stationary reactive state in which reaction goes on forever. In the saturated states the lattice is said to be 'poisoned' with either A or B particles. Mathematically, these are *absorbing* points of the process.

A richer kinetic behaviour is displayed by the monomer-dimer model of Ziff, Gulari and Barshad (ZGB) for the oxidation of carbon monoxide on platinum [4]. The CO is represented by a point particle which adsorbs onto a single lattice site (monomer) with probability p . The adsorption of oxygen molecules require two sites (dimers) and following adsorption the bond in between the O atoms is severed. Adjacent O and CO molecules react to form CO_2 and desorb leaving behind two empty sites. The lattice saturates with O when p is smaller than some critical value p_1 and with CO when $p > p_2$. For all p in between p_1 and p_2 there is a reactive steady state with constant production of CO_2 and finite lattice concentrations of O and CO.

Regarding the lattice concentrations in the long-time asymptotic limit as an order parameter one may speak of dynamical phase transitions at p_1 and p_2 . Varying p from slightly above to slightly below p_2 , the concentration of CO jumps discontinuously from zero to a finite value, marking a first-order transition. Around p_1 , there is a second-order transition which has been shown to belong to the same universality class of directed percolation and Reggeon field theory (RFT) [8, 9].

Dickman [10] has studied a class of models which are lattice realizations of Schlögl's first ($X \rightarrow 0$ and $X \rightleftharpoons 2X$) and second ($X \rightleftharpoons 0$ and $2X \rightleftharpoons 3X$) models, and a more complex 'D₃' model which is similar to Schlögl's second model with an additional annihilation of trimers ($3X \rightarrow 0$). In all these cases, he finds a second-order dynamical phase transition with RFT critical exponents. The other two common features of Dickman's models is that they all consist of a single component and a single absorbing state at the transition point. Indeed, his results support a conjecture by Grassberger [11] that there would always be an RFT type of transition under these two general conditions. Grinstein *et al* [8] have extended this conjecture to multi-component systems, demanding a single absorbing state near the transition point as the sole condition for an RFT type of transition.

Under such general terms, systems that do not belong to the RFT class become the exception rather than the rule and hence are of special interest. In this letter, we present and study a dimer-trimer model for heterogeneous catalysis which displays a phase diagram similar to the ZGB model. However, our model has an infinite number of absorbing states near the transition points, violating the condition for an RFT transition. Our numerical results for the critical exponents of the second-order transition differ markedly from the RFT values, showing that the system belongs to a different universality class.

The dimer-trimer reaction process is symbolically represented by



where '*' denotes an active catalyst site and 'A*' and 'B*' denote chemisorbed particles. The processes (1a) and (1b) are attempted with probabilities p and $1 - p$, respectively. The reaction in (1c) takes place only between nearest neighbours and the product desorbs freeing two lattice sites. In order to avoid spurious effects resulting from asymmetry, we consider the process on a triangular lattice; the trimers

adsorb onto three nearest-neighbour sites constituting the vertices of an equilateral triangle.

Consider the extreme case of $p = 0$. Adsorption of only trimers is attempted. As the lattice fills up, there comes a time when there remain no more triplets of nearest empty sites. At this stage there can be no further adsorption of trimers and the process must stop. Clearly, the final configuration of the lattice is random, depending on the specific history of the individual adsorption events. A similar situation occurs in the opposing limit of $p = 1$. The lattice poisons with dimers into a random configuration with a finite concentration of isolated active sites. This is, in fact, the well known 'car parking' problem [12]. In general, for $0 < p < 1$ absorbing states must also contain only isolated active sites. The absorbing state cannot contain any pair of active sites as long as there is a finite probability for adsorption of dimers. Thus, in analogy with the ZGB model, one expects to find dimer or trimer-poisoned phases but with an infinite number of absorbing states with isolated active sites.

For the actual simulation of the dimer-trimer model on a computer, at each step a dimer (trimer) adsorption is attempted with probability p ($1 - p$). The lattice soon becomes almost completely covered and most adsorption attempts would be rejected. To minimize the time spent on failed adsorptions we keep a list of double empty sites. Adsorption is attempted to sites of this list only. After each trial a 'time' counter is incremented by $1/N$, where N is the total number of empty sites on the list. This corresponds to an average of one attempted adsorption event for every lattice site in one physical time unit. Following each successful adsorption the neighbourhood of the adsorbed particle is checked. Newly formed A-B pairs are removed from the lattice, modelling the reaction and desorption processes. In case of conflicts arising because of more than one way of associating A and B particles, pairs are reacted at random until their complete elimination.

Until now, catalytic reactions have been simulated on conventional scalar computers like the Sun workstations. Because the process of catalysis is not amenable for vectorization we anticipate that vector supercomputers will play no dominant role in future research of this area. We simulated the dimer-trimer process on a Parsytec computer system consisting of 128 parallel transputer units of 4 Mbyte DRAM each. We worked with lattices of up to 500×500 sites evolving the systems for as long as 1000 physical time units. The computation on parallel transputers reduces the total CPU time required dramatically. For example, the computation of the β exponent (see below) was completed in less than 100 hours, while it would have taken 4650 hours on a single transputer. Using a maximum of 108 parallel transputer units we were able to average over ensembles of 10^7 configurations, exceeding other simulations to date by two orders of magnitude.

Our simulations reveal a phase diagram similar to that of the ZGB model, with trimer- and dimer-saturated phases and a steady reaction phase. There is a second-order transition between the trimer-poisoned phase and the reactive phase at $p_1 = 0.3403 \pm 0.0002$, and a first-order transition between the reactive phase and the dimer-poisoned phase at $p_2 = 0.4610 \pm 0.0008$ (figure 1). We notice, as expected, that the absorbing phases contain isolated empty sites. Their final concentration depends on p . Thus, the concentration of empty sites increases from 0.0966 at $p = 0.01$ to 0.106 at p_1 in the trimer-poisoned phase, and from 0.0765 at p_2 to 0.086 at $p = 1$ in the dimer-poisoned phase.

Following Grassberger [13] and Jensen *et al* [9] we performed simulations starting from a trimer-poisoned lattice (with isolated active sites) except for a nearest triplet

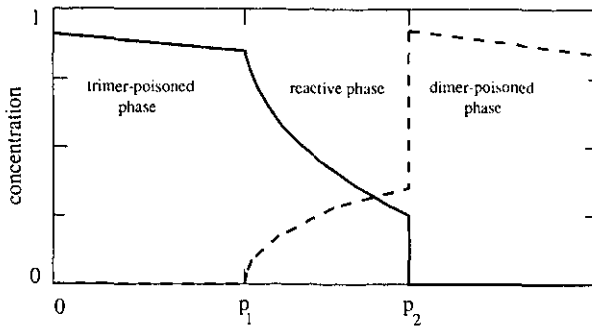


Figure 1. Schematic phase diagram for the dimer-trimer model. The full and broken lines represent the concentrations of trimers and dimers, respectively. The concentration of vacancies equals $1 - c_{\text{dimers}} - c_{\text{trimers}}$. Its variation in the poisoned phases and other features of the phase diagram are exaggerated for clarity.

of empty active sites from which reactions may continue. As the process evolves, this initial seed fluctuates in size until it shrinks and the lattice becomes saturated again. The survival probability at time t , $P(t)$, the average number of sites in the active cluster, $n(t)$, and the *conditional* mean-squared span of the cluster (averaged only over systems that survived until time t), $R^2(t)$, are related to critical exponents through the scaling laws

$$P(t) \sim t^{-\delta} \quad (2a)$$

$$n(t) \sim t^\eta \quad (2b)$$

$$R^2(t) \sim t^z \quad (2c)$$

The 'effective' exponents for timescale t are defined by [9, 13]

$$-\delta(t) = \frac{\ln[P(t)/P(t/\tau)]}{\ln(\tau)} \quad (3)$$

with similar expressions for the other exponents. Here τ is an arbitrary timescale which we chose to be $\tau = 2$. The effective exponents converge to their true value as $1/t$ as $t \rightarrow \infty$ [13]. If p is not exactly equal to p_1 , the asymptotic long-time behaviour of the kinetic quantities in (2) is either faster or slower than the indicated algebraic dependency on t . Thus, plots of the effective exponents against $1/t$ provide a convenient means to estimate both their limiting value and the value of p_1 .

Because the initial absorbing state is not unique in the model, one needs to make a specific choice to proceed with simulations. We overcame this problem by starting each run on different, random configurations of the absorbing state. Thus, the initial state is averaged out at the outset. However, we believe that our results would not be different, had we always started with the same configuration. This is because as the process evolves the cluster of active sites grows, effectively erasing any memory of the initial configuration.

In figures 2(a)–(c), we plot the effective exponents as a function of $1/t$ for various values of p around p_1 . From these data we infer that $p_1 = 0.3403 \pm 0.0002$, and $\delta = 0.40 \pm 0.01$, $\eta = 0.28 \pm 0.01$ and $z = 1.19 \pm 0.01$. The effective exponents should satisfy the hyperscaling relation [13] $\frac{1}{2}dz - \eta \geq 2\delta$, where the equality applies for

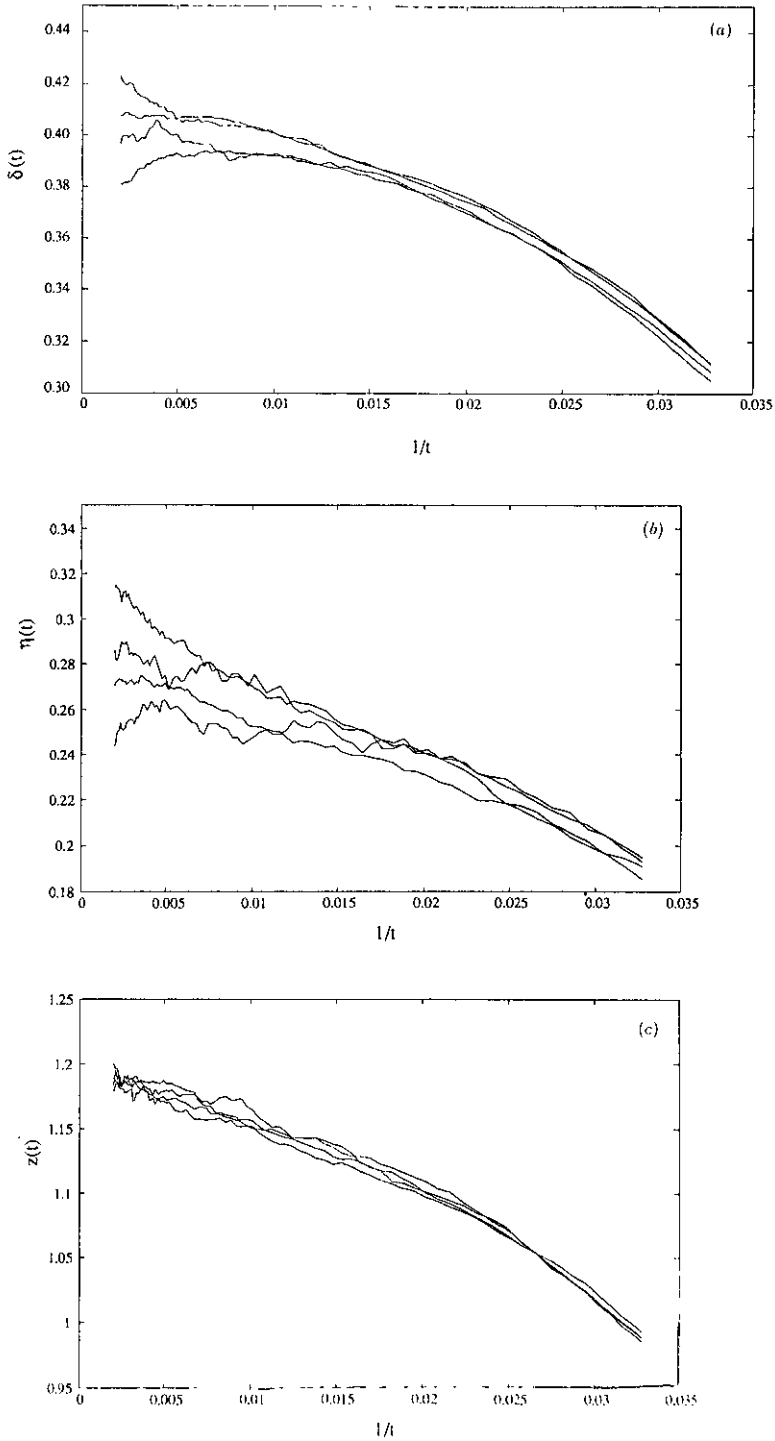


Figure 2. Plots of the effective exponents δ (a), η (b) and z (c) as a function of $1/t$. The curves represent, from top to bottom, data for $p = 0.3998, 0.3402, 0.3404$ and 0.3407 for the δ exponent. The order is reversed for the η and z exponents.

their limiting values at the long-time asymptotic regime. The fact that our estimates above fail to satisfy the equality by a margin of about 10% is of some concern and suggests that the numerical values have not yet converged or that our error bars are not conservative enough. However, even if we enlarged the error bars so as to accommodate the hyperscaling equality, the numerical values of the same critical exponents in RFT [13], $\delta = 0.452 \pm 0.008$, $\eta = 0.214 \pm 0.008$, and $z = 1.134 \pm 0.004$, would still be excluded.

To compute the order-parameter critical exponent, β , we examined the variation of the long-time asymptotic lattice concentrations near the transition point. We have

$$c_A(p) = a(p - p_1)^{\beta_A} \quad (4a)$$

and

$$c_{B,\text{sat}} - c_B(p) = b(p - p_1)^{\beta_B} \quad (4b)$$

where c_A is the concentration of dimers, $c_{B,\text{sat}}$ is the concentration of trimers at the trimer-saturated phase near the transition point, and a and b are constants. Because we used a finite sized lattice, p_1 is not exactly equal to the transition probability of an infinite lattice, but rather an effective transition probability which reflects the finite-size effects.

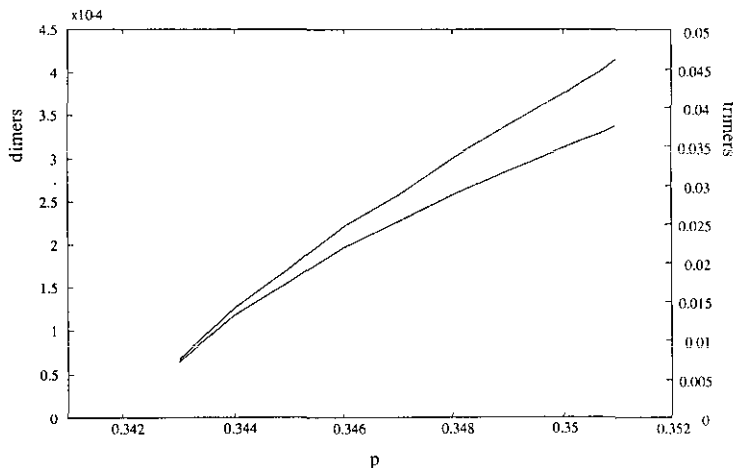


Figure 3. Variation of the concentration of dimers (upper curve) and trimers (lower curve) as a function of the probability p . The β exponent is determined from a numerical best fit to these data (see text).

We measured carefully c_A , c_B and $c_{B,\text{sat}}$ (figure 3), and performed a best fit of the parameters a , b , p_1 , and β_A and β_B . From c_A we find $p_1 = 0.3417 \pm 0.0003$ and $\beta_A = 0.80 \pm 0.06$. From c_B , $p_1 = 0.3420 \pm 0.0003$ and $\beta_B = 0.63 \pm 0.05$. While the effective value of the transition probability agrees in both measurements, the values of the measured critical exponent differ markedly. We have tried other techniques for estimating β but have failed to obtain better accuracy. Our results indicate that β is larger than the 0.58 of RFT [14], but we cannot assert how much larger.

In summary, we have introduced and studied a dimer-trimer model for heterogeneous catalysis. While its phase diagram is similar to the ZGB monomer-dimer

model, it differs in that, rather than one, it has an infinite number of absorbing states at the transition points. This property violates the condition required by the conjecture of Grinstein *et al* for the existence of a second-order phase transition in the same universality class as RFT. Indeed, our numerical results for the transition critical exponents show that the dimer-trimer model is in a different universality class.

Grassberger *et al* [15] have studied a single-component Schlögl-like contact process which has two absorbing states at the transition point and is also not in the RFT universality class. From this and the dimer-trimer model one draws some support for the conjecture of Grinstein *et al*. Perhaps more importantly, the two examples suggest that lattice models for catalysis may span several universality classes other than that of RFT. In the generalized family of j -mer- k -mer models [6], most systems have an infinite number of absorbing states. Their classification into critical universality classes remains an intriguing open question. Other interesting open problems concern the effects of the multiplicity of absorbing states on first-order transitions and on the transient kinetics to the stationary states.

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