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The Dimer–Trimer Model for Heterogeneous Catalysis

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We study a dimer–trimer lattice model for heterogeneous catalysis for the reaction $\frac{1}{2}A_2 + \frac{1}{3}B_3 \rightarrow AB$. The A_2 and B_3 particles require two and three active sites for their adsorption onto the lattice, respectively. The model is unusual in that it possesses an infinite number of absorbing states whereby the lattice is "poisoned" and reactions must stop. Previously studied models have only two absorbing states. In one dimension, the lattice poisons with mostly dimers and a few trimers even at vanishingly small dimer-adsorption probabilities and there is a discontinuity when this probability is zero. On the triangular lattice, the poisoned phases consist of only one component and vacancies, and the phase diagram is similar to that of the monomer–dimer model of Ziff, Gulari, and Barshad. However, the second-order transition belongs to a different universality class than Reggeon field theory, contrary to previous models. Finally, we present results for the Kagomé lattice, for which the poisoned phases consist of two components due to its smaller connectivity.

KEY WORDS: Dimer-trimer model; catalysis.

Catalysis processes which occur on the interface in between two phases, as in the case of gaseous reactants on the surface of a solid catalyst, for example, are termed heterogeneous catalysis. The surface acts as a catalyst by enforcing a physical proximity of the reacting molecules and by weakening the strength of internal chemical bonds crucial to the reaction process, in the source of chemisorption.$^{(1-3)}$ The process is of much practical importance because of its common use in the chemical industry and in controlling toxic emissions into the environment. Traditionally, heterogeneous

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catalysis has been analyzed by mean-field methods, using classical rate equations.(1-3) Recently, it has been realized that microscopic fluctuations and correlations in the concentrations of the reactants have dramatic effects on the kinetics of such systems. Lattice models have been introduced in order to elucidate a wide range of kinetic behavior which was unaccounted for in the classical approach.

A well-known example is 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 A (monomer) which requires a single empty site in order to adsorb. Oxygen molecules are represented by B_2 particles (dimers) which require two sites to adsorb. Adsorption of monomers and dimers is attempted with probability p and $1-p$, respectively. The attempt is rejected unless the target sites are empty. Symbolically,

$$A + * \to A* \tag{1a}$$

$$B_2 + 2* \to 2B* \tag{1b}$$

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

Here the asterisk denotes an active (empty) lattice site and $A*$ and $B*$ denote sites occupied with an A or a B, respectively. The reaction (1c) takes place only between nearest neighbors and AB represents the CO_2 product which desorbs from the lattice, freeing two sites.

In one dimension, the lattice rapidly fills up and eventually completely saturates with either monomers or dimers, depending on whether p is larger or smaller than some critical value, $p_c \cong 0.4$.(4) The saturated states are, mathematically speaking, absorbing points. The process must stop upon reaching either of these two states and the lattice is then said to be "poisoned."

In two dimensions, the lattice saturates with B when p is smaller than some critical value p_1 and with A when $p > p_2$.(4,5) For all p in between p_1 and p_2 there is a reactive steady state in which the lattice concentration of monomers and dimers and the production rate of AB keep constant. Varying p from slightly above to slightly below p_2, the concentration of monomers 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).(6,7)

Dickman(8) has studied a class of models which are lattice realizations of Schlögl's first ($X \to 0$ and $X \rightleftharpoons 2X$) and second ($X \rightleftharpoons 0$ and $2X \rightleftharpoons 3X$) models, and a more complex "D_3" model which is similar to Schlögl's second model with an additional annihilation of trimers ($3X \to 0$). In all these cases, he finds a second-order dynamical phase transition with RFT critical exponents. This supports a conjecture of Grassberger(9) that second-order transitions near a single absorbing state in one-component systems are always in the same universality class as RFT. Grinstein *et al.*(6) generalized this conjecture to multicomponent systems; a single absorbing state near the transition is the only condition for RFT behavior.

In this paper, we present a dimer–trimer model which has an infinite number of absorbing states and analyze it numerically. In one dimension, the lattice poisons mostly with dimers, but with a finite concentration of trimers and vacancies. This holds true for arbitrarily small dimer-adsorption probabilities p, but there is a curious first-order transition at $p = 0$. On the triangular lattice, we find a phase diagram similar to that of the ZGB monomer–dimer model, but the second-order transition is in a universality class different than RFT.(10) Because of the good connectivity of the triangular lattice, the poisoned phases consist of only one component and vacancies. For that reason, we also study the process on the Kagomé lattice, whose smaller connectivity allows for poisoned states with both components.

The dimer–trimer reaction process is symbolically represented by

$$A_2 + 2* \rightarrow 2A* \tag{2a}$$

$$B_3 + 3* \rightarrow 3B* \tag{2b}$$

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

The processes (2a) and (2b) are attempted with probabilities p and $1 - p$, respectively. The reaction in (2c) takes place only between nearest neighbors and the product desorbs immediately following reaction. This corresponds to the adsorption-controlled limit. Other kinetic limits will be studied in future work.

Consider first the process in one dimension. The lattice may poison in an infinite number of ways. The poisoned states contain a finite concentration of single vacancies of the form $\cdots A * A \cdots$, $\cdots A * B \cdots$, $\cdots B * A \cdots$, and $\cdots B * B \cdots$ (here the asterisk represents a vacancy). Thus, a poisoned state generally consists of both components, dimers and trimers, as well as of vacancies.

The limits of $p = 0$ and $p = 1$ are of special interest. They correspond to the random sequential adsorption of trimers or dimers alone, respectively. In the absorbing states, the line is jammed with trimers (or dimers) and vacancies. The jamming concentrations are known exactly. They are $c_{\text{dimers}}(p = 1) = 1 - 1/e^2$ and $c_{\text{trimers}}(p = 0) = 0.823653...$.(11)

If $p = 1 - \varepsilon$ (ε small), then the poisoned state looks nearly the same as the jamming of the line with dimers ($p = 1$), only that occasionally there are some encrusted trimers which managed to survive. These B particles are isolated by single vacancies, thus impeding adsorption of dimers onto the nearest site and a subsequent reaction that would remove them from the lattice. The concentration of trimers is roughly proportional to ε in this regime.

A more peculiar situation occurs near $p = 0$. At $p = 0$ the line jams with only trimers and single and *double* empty sites. The concentration of double empty sizes sites is finite. Thus, for even an arbitrarily small (but positive) probability $p = \varepsilon$, the lattice may adsorb a finite concentration of dimers and there is a discontinuous transition in the value of the poisoning concentrations. In effect, for $p = \varepsilon$ the lattice poisons mostly with dimers. This strange phenomenon is due to the fact that following a reaction two sites are made available and only a dimer can readsorb (unless there was an adjacent vacancy, initially). In this way, long sequences of trimers are replaced by dimers. An analysis of the limit $p \to 0^+$ shows that the vacancies within the trimer clusters cannot effectively stop this process. We cannot provide the exact limiting concentrations at the first-order transition, but we believe these can be computed in a perturbative fashion and using the theory for the jamming of the line with trimers.

In Fig. 1 we present a plot of our simulation results for the concentrations of dimers, trimers, and vacancies as a function of p. The exactly known jamming limits at $p = 0$ and 1 are accurately reproduced by our simulations. Also confirmed are the smooth behavior near $p = 1$ and the

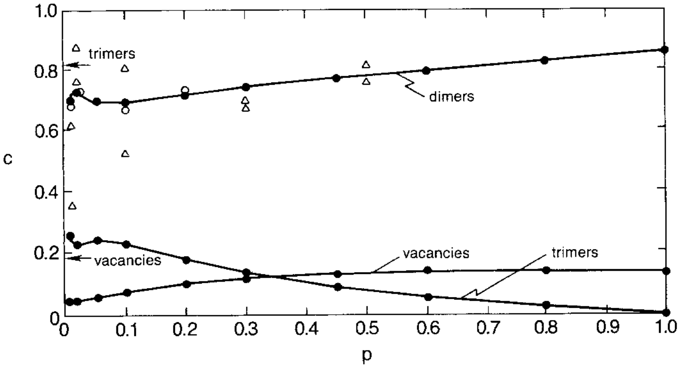

Fig. 1. Phase diagram for the dimer–trimer model in one dimension. The arrows indicate the jump in the concentrations of trimers and vacancies at $p = 0$. The bending of the curves near $p = 0$ is due to finite-size effects. To demonstrate the influence of the lattice size, the dimer concentration is plotted for $L = 10^6$ (solid circles), $L = 10^4$ (open circles), and $L = 10^3$ (triangles).

first-order transition at $p=0$. About the latter, it is interesting that as p gets smaller and smaller, one needs larger lattices and longer times to witness the poisoning. This is because the spreading of dimers starts at a subset of sites whose number (and spacing) is of order $1/p$. The poisoning time scales as $1/p^2$, and lattices of size $L \gg 1/p$ are required for thermodynamically significant results. For smaller lattices, fluctuations dominate and there are strong finite-size effects. We have included results for various lattice sizes to illustrate this point.

The simulations discussed above, as well as other simulations in this paper, were performed on a Parsytec computer system consisting of 128 parallel transputer units of 4 MByte Dram each. Because the process of catalysis is not amenable to vectorization, we anticipate that vector supercomputers will play no dominant role in future research in this area. The simulation of the dimer–trimer model is particularly time-consuming. Working with the Parsytec parallel transputers, we were able to exceed the typical size of other simulations to date by two orders of magnitude (in two dimensions, we worked with 500×500 lattices averaging over 10^7 runs of up to 1000 physical time units each). This turned out to be an essential minimum for obtaining reliable results.

We have also performed a mean-field analysis of the dimer–trimer model in one dimension, based on Dickman's cluster approximation.(12) The two-site approximation fails to reproduce the first-order transition at $p=0$. It is interesting, however, that the two-site approximation yields the exact jamming concentration with dimers $(p=1)$.(12) A three-site approximation gives an exact description of the jamming of the line with trimers. We suspect that it also would suffice to reproduce the first-order transition and are currently checking out this possibility.

We now turn to the model in two dimensions.(10) To achieve maximum symmetry, we consider the process on a triangular lattice; the trimers adsorb onto three nearest neighbor sites constituting the vertices of an equilateral triangle. For very small or very large p we expect poisoning with mostly trimers or dimers, with $p=0$ and 1 being the limits of trimer and dimer jamming, respectively. Notice, however, that the poisoned states on the triangular lattice cannot generally contain both components. In order to prevent a cluster of particles from reacting with the opposing species, it needs to be surrounded by a boundary of empty sites. Adsorption of dimers is always possible onto such a boundary, so that in reality one is unable to segregate dimers and trimers. The poisoned phases contain one component only, although there still is an infinite number of absorbing states due to the possible different distributions of the single vacant sites.

We observe 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 $p_2 = 0.4610 \pm 0.0008$ (Fig. 2). 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.*,(7) we performed an "epidemic" analysis (see also ref. 14) of the second-order phase transition. Starting from a trimer-poisoned lattice except for a patch of empty active sites from which reactions may continue, we monitored 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), $R^2(t)$. These are related to critical exponents through the scaling laws

$$P(t) \sim t^{-\delta} \tag{3a}$$

$$n(t) \sim t^{\eta} \tag{3b}$$

$$R^2(t) \sim t^{z} \tag{3c}$$

These exponents vary with time scale and for $p = p_1$ they converge to their limiting value as $1/t$.(13) In Figs. 3a–3c we plot the effective exponents as a function of $1/t$. The plots achieve the double goal of evaluating p_1 and estimating the numerical value of the exponents.

From our 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 $z = 1.19 \pm 0.01$. These differ from the numerical values

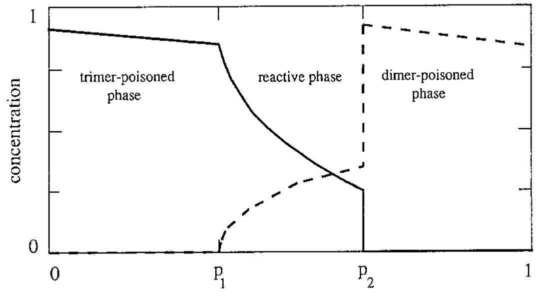

Fig. 2. Schematic phase diagram for the dimer–trimer model on the triangular lattice. The solid and broken lines represent the concentrations of trimers and dimers, respectively. The concentration of vacancies equals $1 - c_{\text{dimers}} - c_{\text{trimers}}$. Its variation in the poisoned phases and other features of the phase diagram are exaggerated for clarity.

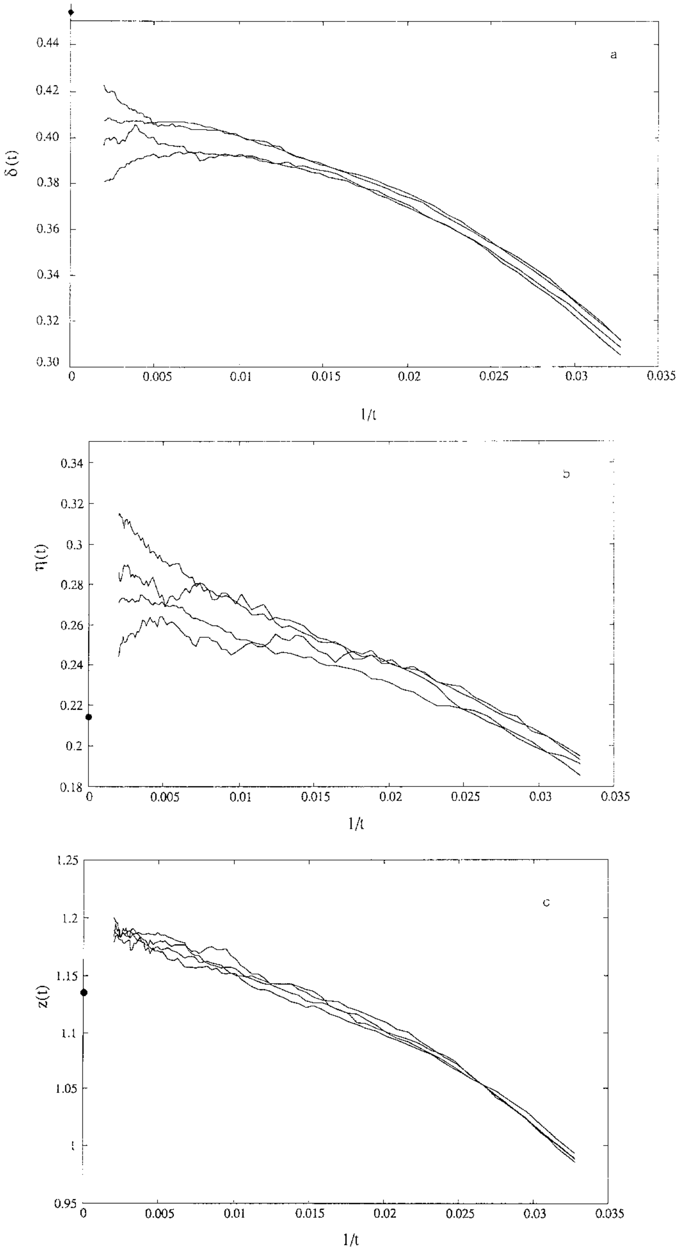

Fig. 3. Plots of the effective exponents (a) δ, (b) η, and (c) z as a function of $1/t$. The curves represent, from top to bottom, data for $p = 0.3998$, 0.3402, 0.3404, and 0.3407 for the δ exponent. The order is reversed for the η and z exponents. The RFT exponents are shown for comparison.

of the RFT critical exponents,(13) $\delta = 0.452 \pm 0.008$, $\eta = 0.214 \pm 0.008$, and $z = 1.134 \pm 0.004$, showing that the dimer–trimer model is in a different universality class. We attribute this difference to the infinity of absorbing states at the second-order transition.

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

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

and

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

where c_A is the concentration of dimers, $c_{B,\mathrm{sat}}$ is the concentration of trimers at the trimer-saturated phase near the transition point, and a and b are constants. We find $\beta_A = 0.80 \pm 0.06$ and $\beta_B = 0.63 \pm 0.05$. This suggests that β is larger than the 0.58 of RFT,(15) but we cannot assert how much larger.

Finally, we examine the dimer–trimer model on the Kagomé lattice. Now one can isolate subsets of the lattice with a boundary consisting of only single empty sites. Segregation into dimers and trimers is possible and poisoning occurs with *both* components. The reduced connectivity of the Kagomé lattice simplifies its mean-field analysis dramatically compared to the triangular lattice. Thus, the numerical results presented below are also important for comparison with future mean -field work.(16)

We obtain a phase diagram somewhat like that of the triangular lattice (Fig. 4). The dimer-poisoned phase contains a small, but finite concentra-

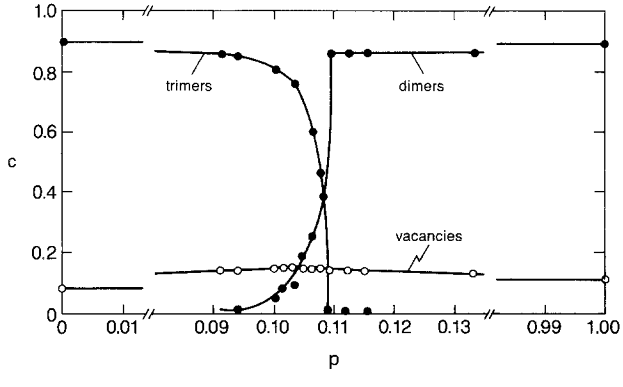

Fig. 4. Phase diagram for the dimer–trimer model on the Kagomé lattice. Data are shown for the concentrations of dimers and trimers (solid circles) and vacancies (open circles). Notice the breaks in the adsorption probability axis.

tion of trimers of the order of $c_{\text{trimers}} \sim 10^{-3}$. The trimer-poisoned phase also contains a small concentration of dimers, $c_{\text{dimers}} \sim 10^{-3}$. The reactive steady state occurs within a narrow window, $p_1 \cong 0.095$ and $p_2 \cong 0.109$. To confirm its existence, we were forced to carry out extensive numerical simulations and to analyze the poisoning times of lattices of varying sizes. The poisoning time scales exponentially with lattice size within the reactive state window.(17)

It is also interesting that the concentration of vacancies is nearly constant for all p, rising slightly at the steady reactive state region, but showing no evident discontinuity at the first-order transition. The increase in the concentration of vacancies in the reactive phase is typical. However, the concentration of vacancies on the triangular lattice is clearly discontinuous near the first-order transition, in contrast to our case. It may be that there is a discontinuity but it is too small to observe comfortably. The concentration of double empty sites shows, indeed, a clear discontinuity, but curiously enough, their concentration in the reactive phase is exceedingly small compared to that on the triangular lattice. Thus, there are intriguing between the processes on the Kagomé and the triangular lattices.

In summary, we have presented and studied a dimer–trimer model for heterogeneous catalysis. Its most novel feature is that it posseses an infinity of absorbing states. In one dimension, poisoning occurs with two components (and vacancies) and there is an unexpected first-order phase transition when the probability for dimer adsorption becomes $p = 0$. On the triangular lattice, poisoning occurs with only one component, but the second-order phase transition between the trimer-poisoned and the reactive phase is in a different universality class thanq that of RFT. On the Kagomé lattice, the dimer-poisoned phase in cludes a small concentration of trimers and the reactive phase occurs within an extremely narrow window of dimer adsorption probabilities.

Grassberger *et al.*(18) have studied a single-component Schlögl-like contact process which has two absorbing states at the transition point and it 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.

The general classification of lattice models for catalysis into universality classes remains an open problem. The mean-field analysis of the dimer–trimer model is a more immediate (and tractable) problem on which we are currently working. Other interesting open questions 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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