Investigation of the first-order phase transition in the A-B_2 reaction model using a constant-coverage kinetic ensemble

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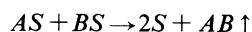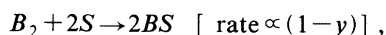*Department of Chemical Engineering, The University of Michigan, Ann Arbor, Michigan 48109-2136*

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The first-order kinetic transition in the A-B_2 (or Ziff-Gulari-Barshad) surface-reaction model [Phys. Rev. Lett. **56**, 2553 (1986)] is investigated using a simulation algorithm (or ensemble) in which the coverage of A is held fixed, while the rate y of A adsorption is allowed to vary. This ensemble allows the metastability loop and spinodal point of the phase transition to be carefully examined. The metastable behavior is found to be in qualitative agreement with the predictions of mean-field theory made by Dickman [Phys. Rev. A **34**, 4246 (1986)]. Furthermore, the transition point is precisely determined to be $y_2 = 0.52560 \pm 0.00001$. The metastable behavior near the spinodal point is also investigated using the standard constant-rate algorithm.

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A few years ago, one of the authors and co-workers introduced a kinetic lattice model based upon the reaction of carbon monoxide (A) with oxygen(B_2) on a platinum catalyst surface. This model, which has become known as the A-B_2 or the Ziff-Gulari-Barshad (ZGB) model [1], shows complex kinetic behavior, and has been studied and modified in many ways [2–10].

In the model's simplest form, diffusion, desorption of reactants, and thermal effects are ignored. Molecules contact the surface randomly and require empty sites in order to adsorb: the A molecules require just one site, while the B_2 molecules require two adjacent (nearest-neighbor) empty sites as adsorption is dissociative. The temperature and pressure of the system are assumed to be such that the kinetics are adsorption limited, so that nearest-neighbor pairs of A and B react and desorb immediately upon formation. The only parameter in the model is y (also called y_A or y_{CO}), defined as the normalized rate (probability) that a molecule making an adsorption attempt is an A. The steps of this model are

$$A + S \rightarrow AS \quad [\text{ rate} \propto y],$$

$$B_2 + 2S \rightarrow 2BS \quad [\text{ rate} \propto (1-y)],$$

$$AS + BS \rightarrow 2S + AB \uparrow$$

$$[\text{rate} = \infty \text{ (for nearest neighbors)}],$$

where S represents a reaction site on the catalyst surface.

In the usual algorithm for simulating these steps on a computer [1], a new molecule impinging on the surface is chosen to be an A with probability y, or a B_2 otherwise. If the molecule is an A, then a single site on the lattice is chosen randomly, and if that site is found to be empty, the A adsorbs there. The four-nearest-neighbor sites are immediately checked in random order; if any B is found, it reacts with the A and the two are removed from the lattice. For a B_2 striking the surface, a nearest-neighbor pair of sites is chosen at random; if both are empty, adsorption of the two B's takes place, and all six-nearest-neighbor sites are checked in a random order for A molecules to react with the B's. In this paper, we call this standard algorithm the "constant-rate" (or constant-y)

ensemble.

When this algorithm is carried out, an ensemble of states reflecting the set value of y is generated. For $y < y_1 \approx 0.387$ [3,4], the system eventually saturates with B, for $y > y_2 \approx 0.5256$ it saturates with A, while for $y_1 < y < y_2$ the system goes to a steady state where reaction continues (nearly) indefinitely. In this reactive state, some A and B molecules remain adsorbed on the surface, along with many empty sites where further adsorption and reaction can take place. At the transition point y_1 the coverages of A and B are continuous functions of y and the transition is termed second-order, while at y_2 the coverages are discontinuous and the transition is first order.

In the past, investigation of the first-order transition has been difficult because of the existence of long-lived metastable states. In order to overcome this problem, we introduce a new "constant-coverage" kinetic ensemble. In the constant A-coverage (constant-Θ) ensemble, the coverage of A is to be kept as close as possible to a desired value, say Θ. This ensemble is achieved by carrying out an A adsorption trial whenever the instantaneous coverage of A (denoted Θ') is less than the set point value Θ, and a B_2 adsorption trial whenever $\Theta' \geq \Theta$. The rest of the procedure—picking one or two sites, checking that they are blank, and checking the neighbors for reactions—remains the same as in the original algorithm. While not every A trial results in an A molecule staying on the surface because of blocking and reaction, eventually one will adsorb without reacting, causing Θ to increase. Likewise, while not all B_2 adsorption trials result in a decrease in Θ, eventually a reaction with an A will occur and Θ will decrease. When the system reaches steady state, one or a few A adsorption trials are carried out, followed by one or a few B_2 trials, back to A, and so on.

We define $\bar{y}$ as the fraction of A adsorption trials to total A and B_2 trials (successful or not). This quantity is the average or effective value of the adsorption rate y corresponding to the given fixed value of Θ. To determine the behavior of the function $\bar{y}(\Theta)$, we ran simulations using the constant-Θ algorithm on a 256×256 square lat-

tice for various values of Θ. The results are summarized in Fig. 1. In the range $0 < \Theta < \Theta_2 \approx 0.075$, the values of $\bar{y}$ as a function of Θ agree with those of the constant-y algorithm. This range corresponds to the stable reactive region in model ($y_1 < y < y_2$). For $\Theta_2 < \Theta < \Theta_s \approx 0.085$, y continues to increase beyond the value at the transition point y_2 to a maximum value of $y_s \approx 0.527$, and the surface contains no unusually large A clusters. However, when Θ is increased beyond Θ_s, a single large cluster appears (as shown in Fig. 2) and the value of $\bar{y}$ begins to decrease. At $\Theta \approx 0.4$, the large A cluster wraps around the periodic boundary of the lattice (much like Fig. 3), and $\bar{y}$ jumps to a value of about 0.5256. As Θ is increased from approximately 0.4 to 0.6, the width of the A-saturated strip increases, but $\bar{y}$ remains nearly constant. For $\Theta \gtrsim 0.7$ the reactive phase ceases to connect around the boundary, becoming just a cluster embedded in the solid A background, and the value of $\bar{y}$ resumes its decline. When $\Theta > 0.90$, the reactive region becomes very small, and $\bar{y}$ is difficult to measure due to fluctuations; we did not study this regime in detail. (Here, a constant B-coverage ensemble may be more appropriate.) In all these simulations, the steady states were found to be independent of the initial state.

The curve in Fig. 1 is effectively the metastability loop for this system, and the point $(\bar{y}_s, \Theta_s)$ is effectively the spinodal point. (Note that there is also a spinodal point for $\Theta \to 1$.) This behavior is very similar to that found from mean-field theory by Dickman [5], who found (using a two-site approximation) a transition at $y = 0.5241$ and spinodal point at $y = 0.5610$. The loop found here is less pronounced than that in the mean-field theory.

We note that the shape of the curve $\bar{y}(\Theta)$ is dependent upon the system size for $\Theta > \Theta_s$. This is because when the system contains a large A cluster, the value of $\bar{y}$ is determined by the size or curvature of that cluster rather than on the value of Θ. As the size of the lattice is increased, the value of Θ which produces a single large

cluster of a given size decreases. Thus, on larger lattices, the states for $\Theta > \Theta_s$ and $y > y_2$ will be moved lower down in Fig. 1, and likewise, the steady states with $\Theta > \Theta_s$ and $y < y_2$ will move upward in that figure.

The relation between the two kinetic ensembles can be seen by the following argument. Consider two large systems, one running the constant-Θ algorithm until a steady state, characterized by a value $\bar{y}$, is reached, and the other using the constant-y algorithm with $y = \bar{y}$. The lattice in the constant-y system is being randomly bombarded with A molecules with probability y and B molecules with probability $1 - y$, with no temporal correlation

FIG. 2. A snapshot of the catalyst surface in the constant-Θ ensemble, with fixed $\Theta = 0.20$. Here and in Fig. 3 the black dots represent lattice sites occupied by A, while both adsorbed B molecules and vacant lattice sites are white.
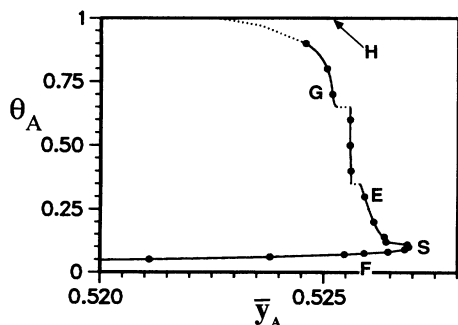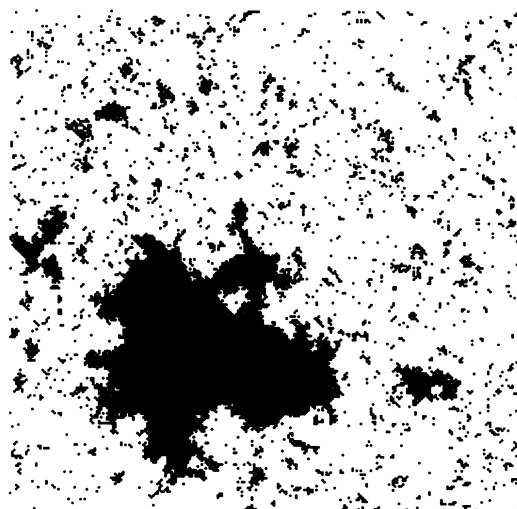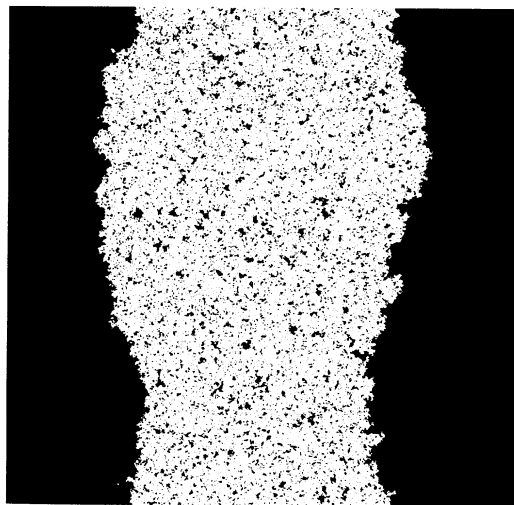

FIG. 1. Enlarged section of the phase diagram of the constant-Θ simulation showing the first-order transition at $y = y_2$, generated from simulations on a 256×256 lattice. Each dot represents a data point, and s marks the spinodal point. Portions of the curve that were not studied in detail are represented by dotted lines. As described in the text, the shape of the metastability loop for $\Theta > \Theta_s$ depends on the size of the system used: for larger systems, the points E and G approach the points F and H, respectively, along lines of constant $\bar{y}$.

FIG. 3. A snapshot of a 1024×1024 lattice in the constant-Θ ensemble with fixed $\Theta = 0.5$ in steady state, used to determine y_2. Periodic boundary conditions were used in both directions.

between these two events. The lattice in the constant-Θ system is also being bombarded with A and B molecules with the same probabilities (since $y=\bar{y}$), but these events are correlated over short times due to the nature of the constant-Θ algorithm. However, if one considers just a small patch of the constant-Θ surface, then this correlation between successive adsorption attempts will not be seen, since it is unlikely that successive adsorption attempts will take place in same small region of the lattice. The A and B_2 molecules will therefore arrive at the patch essentially randomly. Thus we conclude that the adsorbed molecules on the patch of the constant-Θ system will assume a steady state of the corresponding constant-y system.

When $\Theta < \Theta_s$ and $y < y_s$ (no large clusters), the argument given above predicts that the function $\bar{y}(\Theta)$ of the constant-Θ ensemble should be equivalent to $\bar{\Theta}(y)$ of the constant-y ensemble, as verified in our simulations. But when $\Theta > \Theta_s$, a large A cluster forms on the lattice, and there are three regions where we could choose to locate the small patch: (1) wholly in the reactive phase, (2) wholly in the adsorbed A cluster, and (3) on the boundary between the adsorbed A cluster and the reactive phase. All three of these locations must correspond to steady states (stable or metastable) in the constant-y algorithm.

To elucidate this point, we ran additional simulations using the conventional constant-y algorithm at fixed $y=0.526$, using both 256×256 and 512×512 lattices. This value of y is above the transition point y_2, but below the spinodal point $\bar{y}_s$. First, simulations on an initially vacant lattice were carried out for over 100 000 Monte Carlo steps (MCS) each. Here, the system always attained the low-Θ (reactive) steady state, and the largest A clusters that appeared were less than 30 sites across. Next we chose as the initial state a circular island of A, formed by setting all sites within a distance r of the center of the lattice equal to A, and leaving the other sites initially blank. When $r<60$, the initial A island always shrank and disappeared within 5000–20 000 MCS, with the system ending up in the low-Θ_A steady state. However, for $r>70$, the clusters always grew and the system saturated with A within 100 000–150 000 MCS. For $60<r<70$, the system sometimes went to the A-saturated state and sometimes went to the reactive steady state. A total of 25 runs were carried out.

Thus we see all three steady states available to the constant-y system: the reactive steady state with no large clusters, a metastable state in which a large cluster exists, and a steady (poisoned) state with all A. Which state the system goes to depends primarily upon the initial conditions. If the system is initially blank or contains only small A clusters, then the system will almost always go to a reactive steady state, which, for this value of y, is metastable (but apparently with a very long lifetime). If the system contains a critical cluster, then it is in an unstable steady state, and small fluctuations will drive it to one of the two stable steady states. Finally, if the system contains a cluster larger than the critical size, it will almost always go to the poisoned state. These three steady states correspond to the three values of Θ in the phase diagram

in Fig. 1 corresponding to $y=0.526$.

The small patch argument implies that the large A cluster which forms in the constant-Θ ensemble for a given $\Theta > \Theta_s$ is a typical unstable critical cluster in the constant-y ensemble with $y=\bar{y}$. To show this, we ran the constant-Θ ensemble on a 256×256 lattice with $\Theta=0.20$, and at steady state the value $\bar{y}=0.526\,12$ was found. (The cluster formed is shown in Fig. 2). This surface was then used as an initial condition for a series of constant-y simulations with $y=\bar{y}=0.526\,12$, and indeed, the system was found to saturate with A or go to the reactive steady state with equal probability.

The existence of metastability in the system explains why different investigators who used a blank initial lattice found different values for y_2: Meakin and Scalapino [3] found the value 0.5277 ± 0.0002 using a 512×512 lattice, while Yaldram and Sadiq [6] found $y_2=0.5255\pm0.0005$ using a lattice 40×40. This discrepancy can be attributed to the different system sizes, which determined how close each simulation could approach the spinodal point before a cluster of critical size nucleated, triggering the transition to the A-poisoned state. The lattice in Meakin and Scalapino's simulations was large enough so that they essentially found the spinodal point (although at a slightly higher value than found here), while Yaldram and Sadiq's lattice was sufficiently small so that the boundary could help the nucleation process. Because the latter authors happen to choose a lattice size not much larger than a typical cluster at the transition point, they found a value of y_2 consistent with the actual transition point.

In order to determine the true transition point, an interface between the phases must exist. This interface should be roughly flat or without net curvature, since y_2 is effectively the value at which an infinite A cluster grows or shrinks with equal probability. Such a flat interface can be formed in the constant-Θ ensemble by fixing Θ near 0.5, so that the phase boundary wraps around the system (because of periodic boundary conditions). We thus carried out a simulation of the constant-Θ algorithm on a 1024×1024 lattice, with $\Theta=0.5$. To speed up the warm-up, we initially placed a 1024×512 rectangle of A on the lattice, leaving the other sites vacant. The value of $\bar{y}$ appeared to reach steady state (as shown in Fig. 3) after the system was allowed to run for 10 000 MCS. Running the simulation for an additional 205 000 MCS, we found $\bar{y}=y_2=0.525\,60\pm0.000\,01$, with the error bars representing the measured sample error. This value is consistent with, but significantly more precise than, previous determinations in which nucleation was not a problem [1,7]. Note that, while we chose to run this simulation at $\Theta=0.5$, any value of Θ in the range 0.4–0.6 (on this size lattice) could have been used, as long as an A cluster formed that wrapped around the system to form a flat interface between phases.

Finally, the constant-Θ ensemble is also very useful for studying the ZGB model with spontaneous desorption of species A, which has been studied previously using the constant-y ensemble [9,10]. Running the constant-Θ algorithm with various values of the desorption probability P_{des} (the rate of desorption divided by the combined rate
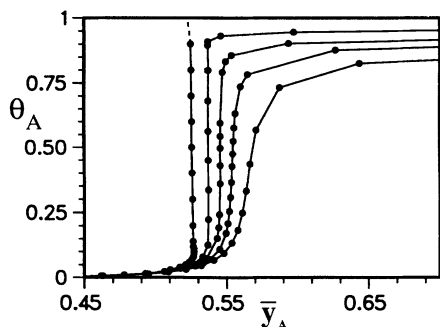
FIG. 4. Enlarged section of the phase diagram of the constant-Θ model with spontaneous A desorption on a 512×512 lattice. The curves represent, from left to right, $P_{des} = 0$, 0.03, 0.05, 0.07, and 0.10. Each dot represents the results of a separate simulation. When $P_{des} < P_c \approx 0.04$, slight metastability loops were observed, but are not visible in this plot.

of A and B adsorption attempts), we find the behavior shown in Fig. 4. When P_{des} is small, the system still exhibits phase separation, one phase being high in Θ, and the other low. When P_{des} is greater than a critical value of ≈ 0.04, the first-order phase transition does not occur. Our results agree with those of a recent study of Tomé and Dickman [8], who also find a critical value of P_{des} slightly above 0.04. We note that in experimental observations of the oxidation of CO, a smoothed-out first-order transition, similar to what is seen here with a nonzero P_{des}, is observed [10]. Furthermore, it has been shown that the existence of a rapidly decreasing reaction rate with increasing y about this transition point—as seen here—is essential for the occurrence of kinetic self-sustained oscillations [11].

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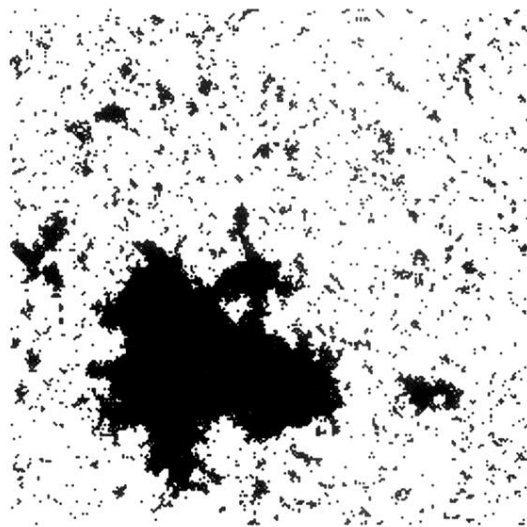FIG. 2. A snapshot of the catalyst surface in the constant-Θ ensemble, with fixed Θ = 0.20. Here and in Fig. 3 the black dots represent lattice sites occupied by *A*, while both adsorbed *B* molecules and vacant lattice sites are white.
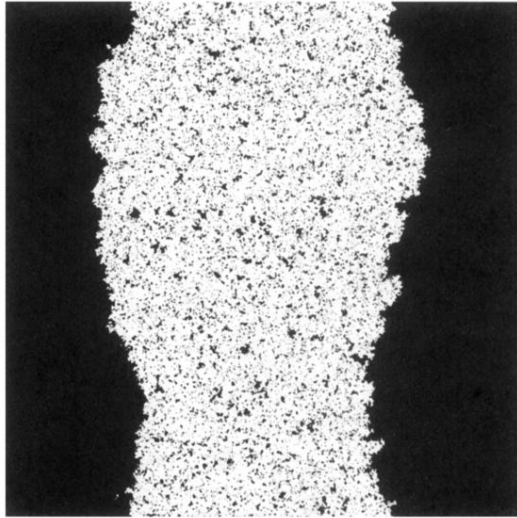
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