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COMMENT

Cellular automaton version of the AB_2 reaction model obeying proper stoichiometry

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Abstract. The cellular-automaton (CA) AB_2 surface-reaction model of Chopard and Droz is modified so that the proper stoichiometry in both the B_2 adsorption and the AB reaction is followed. Simulations show that the first-order kinetic phase transition of the Monte Carlo AB_2 model is recovered. A mean-field analysis, which predicts a first-order phase transition, is also presented.

1. Introduction

A few years ago, Chopard and Droz [1] (CD) introduced a cellular-automaton (CA) version of the AB_2 surface reaction model, which shows qualitatively different behaviour than the Monte Carlo AB_2 model of Ziff, Gulari and Barshad [2] (ZGB). In the ZGB model, the system was found to undergo both second- and first-order kinetic phase transitions as the parameter $y = y_A$ (the proportion of A trials) was increased. In the CD implementation of this model for a CA, the system was still found to go through two 'poisoning' transitions; however, both transitions were second-order. In the second-order transitions, the coverages of A and B (θ_A and θ_B) are both continuous functions of y , while in the first-order transition, the coverage of A is discontinuous.

In the model of CD, an extra precursor state, C, is added to the three states (A, B and V = vacant) of the ZGB model. A C site turns into a B in the next time step if it has at least one C neighbour; otherwise, it reverts back to V. An A site reacts and desorbs (becoming a V) if it has at least one B neighbour, while a B reacts and desorbs if it has at least one A neighbour. A V becomes an A with probability y and a C with probability $1 - y$. These rules, which are applied simultaneously to all the lattice sites, are described in more detail in [1].

In the ZGB model [2], a B_2 molecule requires two adjacent V sites for the B_2 to dissociate and adsorb, creating two B sites. In the CD model, the C state is introduced to approximate this requirement for a CA. The C state allows an extra time step for the system to determine that there are *at least* a pair of neighbouring V sites before putting down B's. However, as pointed out by CD, the rules are not quite stoichiometric: three B's can adsorb in a triplet of neighbouring C sites, for example. Furthermore, the CD model does not generally show proper stoichiometry in reaction, since it will allow a neighbouring triplet BAB to react and desorb, for example.

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In this lack of strict stoichiometry in B_2 -adsorption and AB-reaction the reason that the transition at the higher y is second order? Or perhaps is this behaviour a result of the processes being carried out as a CA? To resolve this question, we consider a modification of the CD model in which the strict stoichiometry of both two-site processes, namely $C+C \rightarrow BB$ and $A+B \rightarrow VV+AB\uparrow$, is followed.

2. The model

To the CD model we add a vector field at every site in the lattice. This field is simply an arrow that can point in any of the four possible directions, and its direction is assigned randomly to each A, B or C site at each time step. The two-site processes are only carried out on those pairs of sites in which the arrows point toward each other. For example, a C site turns into a B site only if the site to which its arrow points is also a C, and the latter site's arrow points back to the original C. When the arrows of a pair of nearest-neighbour sites point like this, we call it a matching nearest-neighbour (MNN) pair. If a site is an A or B, we desorb it (change it to a V) only if there is a MNN of the opposite species. Clearly, when these rules are applied simultaneously over the whole lattice, only pairs of B molecules will adsorb and pairs of AB molecules will react.

The rules can be summarized as follows:

$$\begin{aligned}
 A &\rightarrow \begin{cases} V & \text{if MNN B} \\ A & \text{otherwise} \end{cases} \\
 B &\rightarrow \begin{cases} V & \text{if MNN A} \\ B & \text{otherwise} \end{cases} \\
 V &\rightarrow \begin{cases} A & \text{with probability } y \\ C & \text{otherwise} \end{cases} \\
 C &\rightarrow \begin{cases} B & \text{if MNN C} \\ V & \text{otherwise} \end{cases}
 \end{aligned}$$

and where the directions of the arrows on all A, B and C sites are assigned when the sites are created, and (for remaining A's and B's) reassigned at each time step. We have carried out simulations of this model on a 64×64 lattice with periodic boundary conditions, and have found that the system undergoes both the first-order and second-order phase transitions of the original zGB model. The transition points are at $y = y_1 = 0.0495$ for the second-order transition, and $y = y_2 = 0.0546$ for the first-order transition. These transition points are much below the values in the zGB model (0.3907 [3] and 0.5256 [4], respectively), a consequence of the much lower effective probability of B_2 adsorption here. Other than this rescaling in transition points, the phase diagram is very similar to that in [1].

In this model, the reaction rate is no longer effectively infinite as it is in the zGB and CD models, since reaction will occur only if the arrows of a neighbouring AB pair point toward each other, and this will occur with a probability of only 1/16. Thus, neighbouring AB pairs can coexist for a number of time steps. Studies of the zGB model with a finite reaction rate [5] show that the phase diagram is not qualitatively changed, except when the reaction rate is very low. Likewise, the adsorption of B_2 is effectively slowed down, since a majority of C's do not have matching arrows and turn

back into V sites. We note that the model can be generalized further by making any of these processes occur at a lower rate, by adding a probability (less than unity) that they will be carried out. It can also be modified by removing the V state altogether, and having newly-vacated sites immediately become A's and C's with the appropriate probabilities. This modification will speed up the reaction process, and make the model more closely approximate the reaction-limited case where vacant sites are quickly filled with reactants. Note that some other CA reaction models are also given in [6].

3. Mean-field analysis

As shown by Dickman [7], much can be learned from mean-field analyses of surface-reaction models. Here we consider the one-site approximation of our CA model, in which case the surface coverages θ_A , θ_B , θ_C and θ_V satisfy the following equations:

$$\frac{d\theta_A}{dt} = y\theta_V - \frac{1}{4}\theta_A\theta_B \quad (1)$$

$$\frac{d\theta_B}{dt} = \frac{1}{4}\theta_C^2 - \frac{1}{4}\theta_A\theta_B \quad (2)$$

$$\frac{d\theta_C}{dt} = (1-y)\theta_V - \theta_C \quad (3)$$

$$\theta_V = 1 - \theta_A - \theta_B - \theta_C. \quad (4)$$

These equations reflect the change in the system in one cycle of the CA. The first term on the RHS of (1) gives the gain in θ_A due to adsorption, while the second term represents the loss due to AB reactions. In the latter term, the factor θ_A reflects the probability that the given site is an A, the factor θ_B reflects the probability that the site pointed to by the A-arrow is a B, and the factor of 1/4 represents that probability that the arrow on the B points back to the A. Likewise, the two terms in (2) represent the gain in θ_B due to adsorptions, and the loss due to reactions, respectively. Equation (3) says a V can become a C with probability $1-y$, and an existing C disappears with probability 1 (since it always becomes either a B or a V). Finally, (4), closes the equations with the conservation of sites.

Setting the time derivatives equal to zero, we find the steady-state coverages

$$\begin{aligned} \bar{\theta}_C &= \frac{4y}{1-y} & \bar{\theta}_V &= \frac{4y}{(1-y)^2} \\ \bar{\theta}_{B,A} &= b \pm (b^2 - \bar{\theta}_C^2)^{1/2} & b &= (1 - \bar{\theta}_C - \bar{\theta}_V)/2 \end{aligned} \quad (5)$$

where $\bar{\theta}_B$ corresponds to the positive root and $\bar{\theta}_A$ to the negative root. These equations are valid for $y < y_s = (9 - 2\sqrt{17})/13 \approx 0.057984$, which represents the spinoidal point in the system. At y_s , $\bar{\theta}_A = \bar{\theta}_B = \bar{\theta}_C = 2\sqrt{17} - 8 \approx 0.246211$. The behaviour of $\bar{\theta}_A$ and $\bar{\theta}_B$ as a function of y is qualitatively similar to behaviour of the one-site mean field model given by Dickman [7]. The existence of a spinoidal point suggests that there is a first-order phase transition at a value of y somewhat below y_s . Indeed, the CA transition point $y_2 = 0.0546$ is just below the mean-field spinoidal point.

To understand the behaviour of the mean-field system about the steady-state, one can linearize (1)-(4) about (5), and solve for the eigenvectors and eigenvalues of the

system. This analysis shows that the fastest mode is essentially of $\theta_C \rightarrow \bar{\theta}_C$, the intermediate mode is for $\theta_V \rightarrow \bar{\theta}_V$, and the slowest mode is for $\theta_A \rightarrow \bar{\theta}_A$ and $\theta_B \rightarrow \bar{\theta}_B$.

We finally note that this mean-field model does not depend upon the system being a CA. It also applies to an AB_2 model in which the reaction occurs with a finite rate, and only one direction is checked for occupation by a molecule of the opposite species, at each reaction trial. The factors of 1/4 would have to be replaced by constants representing the appropriate adsorption and reaction rates.

Thus, we conclude that it is the lack of proper stoichiometry for two-site processes in the CD model that is responsible for its (high- y) second-order phase transition. We have shown that it is possible to devise a CA version of the AB_2 reaction that qualitatively agrees with the Monte Carlo formulation (the ZGB model).

Acknowledgments

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