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A mean-field approximation scheme containing the spatial parameter and its application to a surface-reaction-like cellular automaton model

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Using an AB_2 surface-reaction-like cellular automaton model, we present a modified mean-field approximation scheme for describing some dynamic lattice models, in which a lattice freedom parameter N is introduced as a variable. We obtain the phase diagrams of the example model for linear, hexagonal, square and triangular lattices, and we reveal a second-order phase transition which has not been found using traditional approaches.

Keywords: mean-field scheme, dynamic lattice model, phase transition
PACC: 0520D, 0550, 0570F

1. Introduction

Lattice models have been proven to be effective in studying the kinetics of catalytic surface reactions (CSRs).[1−11] Computer simulations of such models have revealed many interesting behaviours such as kinetic phase transitions (for a review of these studies, see Ref.[12]). Despite their apparent simplicity, however, computer simulations may easily become extremely laboured using a reaction model with increasing complexity or which changes slightly. Moreover, simulation results remain to be understood on a conceptual base. Therefore, theoretical approaches need to be developed which can describe CSRs more efficiently and with a more direct predictive power.

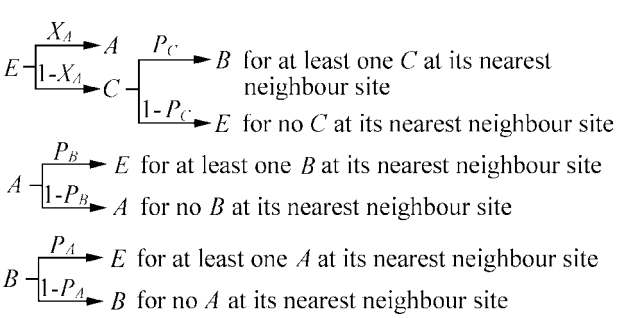
Traditionally, the kinetics of a CSR is analysed with the help of rate equations (a mean-field scheme with site approximation) concerning the time evolution of average coverages of adsorbed molecules on the catalytic surface. In this scheme, a pair probability involved in a two-site process (such as the dimer's adsorption or the reaction between different species) is usually approximated by the product of two site probabilities (denoted as $\theta_{ij} = \theta_i\theta_j$, known as the Bragg–William (BW) approximation). Some important features based on spatial correlation or local fluctuations are missing in this simplest approximation. For example, though the rate equations in the BW approximation have correctly predicted the first-order dynamic phase transition of the AB_2 surface reaction model, they failed to find the second-order transition of the model.[13,14] In order to describe CSRs more accurately, some higher-order approximation mean-field schemes have been developed in which the pair probability[13] or cluster probability[15] is used as a variable. Despite their better accuracy than the former in describing CSRs, these schemes are not often applied to other models due to their complication. In fact, site approximation is still widely used to obtain a quick impression of the behaviours in a system, or to give a simple explanation of some computer simulated results (for examples of other systems, see Refs.[16]–[18]). In this paper, we present a more general way to represent the pair probability in the framework of a site-approximation mean-field scheme, in which the spatial parameter is introduced as a variable in the theory. We use a surface-reaction-like cellular automaton (CA) model to illustrate this method. The model reaction considered is of monomer–dimer (AB_2) type: $A+\frac{1}{2}B_2 \rightarrow AB$, which is known as a prototypical surface reaction and has sufficient simulated results[1,19] for reference.

In the following sections, we first give a description of the AB_2 surface-reaction-like CA model on a general lattice. Then we introduce a mean-field approximation scheme containing a lattice freedom parameter N. After some results are sorted, we make some remarks on the results and the method.

2. Model

We use a CA model to show our method. CA models describe a universe consisting of many discrete 'cells' (lattice sites). Each site is endowed with a finite number of states, and all the sites update their states simultaneously at one time step according to a uniform local rule. Serving as simple models that describe a class of non-equilibrium dynamical systems, CA models have been used to investigate a variety of physical, chemical and biological systems.[20−23]

The present model is similar to that proposed by Chopard and Droz[24] but in a more general way. We consider a general lattice on which each site has N nearest neighbours. For a regular lattice, N can have values of 2, 3, 4 and 6 for linear, hexagonal, square and triangular lattices, respectively. The structures of hexagonal and triangular lattices are shown in Fig.1. Above the lattice are the mixed gas-phase molecules A and B_2 with concentrations of X_A and $X_B = 1 - X_A$ respectively. Each lattice site may be in one of the following three states: A, B and E, meaning A-occupied, B-occupied and empty states, respectively. All the site states update themselves simultaneously at one evolution step according to the following local rules. (1) E transforms into A with a probability X_A, or a conditional occupied state C with a probability 1-X_A. This C immediately turns into B in the case of another C being found at its nearest-neighbour sites; otherwise it turns back to E. (2) A (or B) transforms into E when there is at least one B (or A) at its nearest neighbours; otherwise it remains invariable. Note that in this model C is a fictitious state describing the impingement of B_2 on the lattice, and the processes proceeding on the lattice are at an adsorption limit (infinite reaction rate). The steps of the model are formulated as follows:



The symbols above the arrows denote the transformation probabilities.

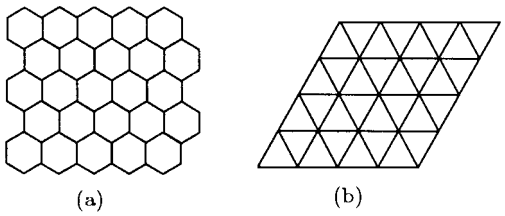


Fig.1. The structures of hexagonal (a) and triangular (b) lattices defined in this paper.

3. Theory

3.1. Rate equations and the BW approximation

In the rate equations, the variables used are the average coverage fractions θ_X (X=E, A, B or C). From the CA rules described above, one has

$$\frac{\mathrm{d}\theta_A}{\mathrm{d}t} = \theta_E X_A - \theta_A P_B, \tag{1}$$

$$\frac{\mathrm{d}\theta_B}{\mathrm{d}t} = \theta_C P_C - \theta_B P_A, \tag{2}$$

where $\theta_C = \theta_E(1 - X_A)$ and $\theta_E = 1 - \theta_A - \theta_B$.

The traditional choice of transformation probabilities is that P_X=θ_X (X = A, B or C), as in Refs.[14], [25] and [26] etc. In this choice, the pair coverage fractions are approximately represented as $\theta_{AB} = \theta_A\theta_B$ and $\theta_{CC} = \theta_C^2$, known as the BW approximation which is independent of the structure of the lattice and thus involves no spatial correlations in the system. At this lowest-order approximation, the equations correctly predict the first-order transition between the A-saturated and the steady reactive phases (SRPs), but fail to find the B-saturated phase and the second-order transition between this and the SRP.

3.2. New choice of approximation

In this subsection, we first present a general way of choosing the transformation probability P_X. Then we prove that at the adsorption limit (infinite reaction rate) the correct choice of transformation probability is $P_X = 1 - (1 - \theta_X)^N$, and only in the case of finite reaction rate (the reaction limit) may the traditional choice $P_X = \theta_X$ be suitable.

We consider a cluster on the lattice, which contains a central site and N nearest neighbours. A state distribution of these nearest neighbours, which, for example, contains i empty states, j A-states and $(N-i-$

j) B-states, may be denoted as $\{iE, jA, (N-i-j)B\}$, where i=0, 1, ..., N and j=0, 1, ..., $N-i$. For such a distribution there are $\frac{N!}{i!j!(N-i-j)!}$ possible configurations. An example $\{3E, 0A, 1B\}$ and its possible configurations are shown in Fig.2.

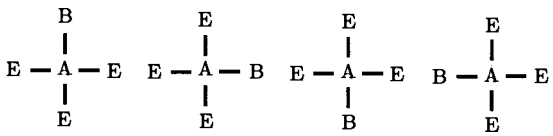


Fig.2. An example for a square lattice (N=4) in a cluster (the central site is supposed to be in the A-state). The nearest-neighbour distribution $\{3E, 0A, 1B\}$ contains four configurations.

In the site approximation, the probability of finding such a distribution may be described by

$$P(i,j) = \frac{N!}{i!j!(N-i-J)!}\theta_E^i\theta_A^j\theta_B^{(N-i-j)}, \qquad (3)$$

with the normalization condition being $\sum_{i=0}^{N}\sum_{j=0}^{N-i} P(i,j)$ $= (\theta_E + \theta_A + \theta_B)^N = 1$.

Because we are concerned with whether there are species X ($X = A, B$, or C) in the nearest neighbours to interact with the central site, we may simplify the above probability as

$$P(k) = \frac{N!}{k!(N-k)!}\theta_X^k(1-\theta_X)^{(N-k)}. \qquad (4)$$

This is the probability of finding kX states together with $N-k$ others in the nearest neighbours, and is limited by the condition $\sum_{k=0}^{N} P(k) = 1$.

In the adsorption limit (infinite reaction rate) as considered in the present model, the transformation probability (for at least one X at the nearest-neighbour sites) may easily be obtained

$$\begin{aligned} P_X &= \sum_{k=1}^{N} P(k) \\ &= \sum_{k=0}^{N} P(k) - P(0) = 1 - (1-\theta_X)^N. \end{aligned} \qquad (5)$$

However, if the reaction rate is finite, say, each nearest-neighbour X has a probability $\frac{1}{N}$ to react with the central site, then the transformation probability is given by

$$\begin{aligned} P_X &= \sum_{k=1}^{N} \frac{k}{N} P(k) \\ &= \theta_X \sum_{k=1}^{N} \frac{(N-1)!}{(k-1)!(N-k)!}\theta_X^{k-1}(1-\theta_X)^{N-k} = \theta_X. \end{aligned} \qquad (6)$$

4. Results

4.1. Phase diagrams

Using Eq.(5) instead of the BW approximation, the rate equations for the present model may be formulated as follows:

$$\frac{\mathrm{d}\theta_A}{\mathrm{d}t} = \theta_E X_A - \theta_A[1-(1-\theta_B)^N], \qquad (7)$$

$$\frac{\mathrm{d}\theta_B}{\mathrm{d}t} = \theta_C[1-(1-\theta_C)^N] - \theta_B[1-(1-\theta_A)^N], \qquad (8)$$

$$\theta_C = \theta_E(1-X_A), \qquad (9)$$

$$\theta_E = 1 - X_A - \theta_B. \qquad (10)$$

Numerical integrations of Eqs.(7)–(10) are carried out, starting from θ_E=1 and θ_A=θ_B=0. The results are shown in Figs.3(a)–3(d).

For N=6 (triangular lattice), N=4 (square) and N=3 (hexagonal), the model exhibits three phases which are the A-saturated and two SRPs. The SRP in the smaller X_A region is a lower active phase with a smaller production rate (we denote such a phase as low-SRP), while that in the larger X_A region (denoted as high-SRP) is a higher active phase with a larger production rate. The transition between the high-SRP and the A-saturated phase is of first order (discontinuous), while that between the low-SRP and the high-SRP is of second order (continuous). As the lattice freedom parameter N decreases, the window of the high-SRP becomes narrower and narrower, until it disappears for N=2. The transition values for different N are presented in Table 1. The overall phase structure is in good agreement with that observed from computer simulations[1] except for the low-SRP which takes the place of the B-saturated phase in the small X_A region.

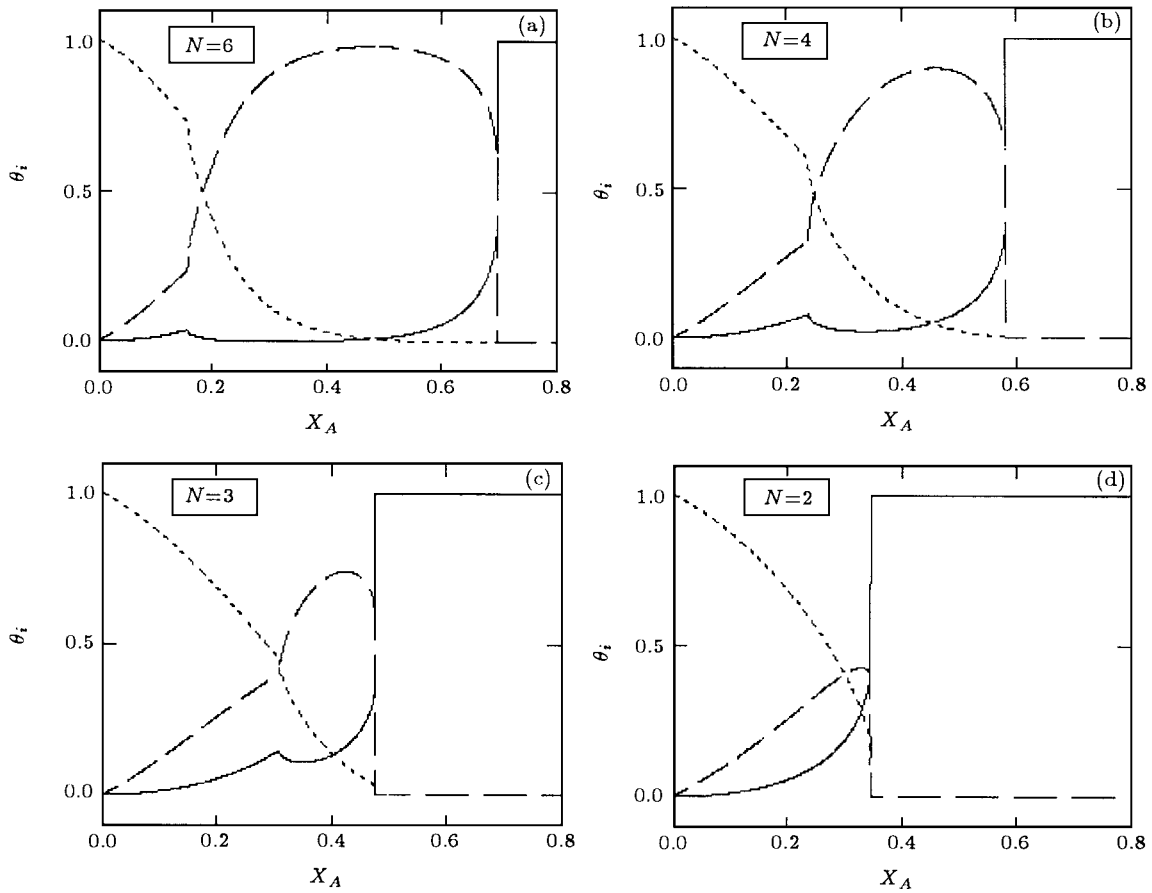


Fig.3. Phase diagrams of the AB_2 surface-reaction-like CA model on (a) triangular, (b) square, (c) hexagonal and (d) linear lattices. The average coverages θ_A (——), θ_B (- - - - -), and θ_E (— —) vary as functions of X_A.

Table 1. The second-order (X_{A1}^C) and first-order (X_{A2}^C) transition values for different values of lattice freedom N.

N	6	4	3	2
$X_{A1}^C(\pm 0.001)$	0.155	0.236	0.309	—
$X_{A2}^C(\pm 0.0005)$	0.6955	0.5785	0.4765	0.3445

4.2. Further analysis of the low-SRP

The behaviours of the low-SRP deserve to be further discussed.

(1) In this phase state, B has a high coverage while A takes a much lower fraction of the lattice. The coverages θ_E, θ_A and θ_B are very weakly dependent on the lattice freedom parameter N (see Fig.4), compared with that in the high-SRP. To understand such behaviours, we examine the production rate of this phase, and find that θ_A and its decrease ($\theta_A^- = \theta_A[1-(1-\theta_B)^N]$) almost identify with each other (see Fig.5). This implies that, for small X_A in a steady state, nearly each of the A states on the lattice is neighboured by B states, and thus the geometric factor of the lattice structure plays little role in dynamics. While with X_A approaching the critical value, the geometric factor begins to play a significant role and a second-order transition occurs.

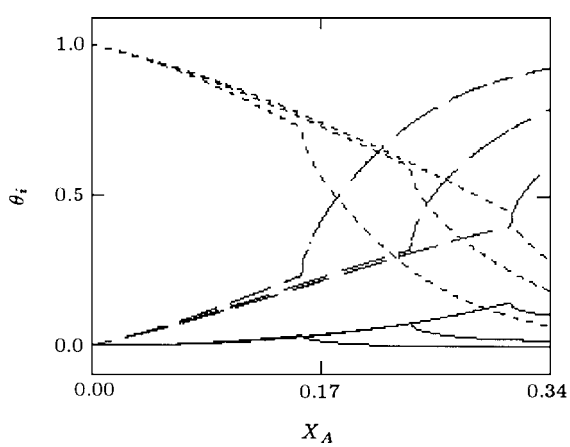


Fig.4. Coverages θ_A (——), θ_B (- - - - -), and θ_E (— —) for N=6, 4 and 3 respectively. In the region $0 < X_A < X_{A1}^C(N)$, they are very weakly dependent on N.

(2) The theory cannot predict the B-saturated phase observed in computer simulations, instead a low-SRP emerges. Such a behaviour may be attributed to the site-approximation mean-field feature.

Note that the spatial correlations in the two-site processes (dimer adsorption and the reaction between A and B) are averaged out and no local fluctuations are taken into account in this theory. The higher-order approximation (such as pair or cluster approximations[13,15]) theory can predict the B-saturated phase. Such a phase can even be observed in the site-approximation framework when fluctuations are introduced into the simulation.[27,11]

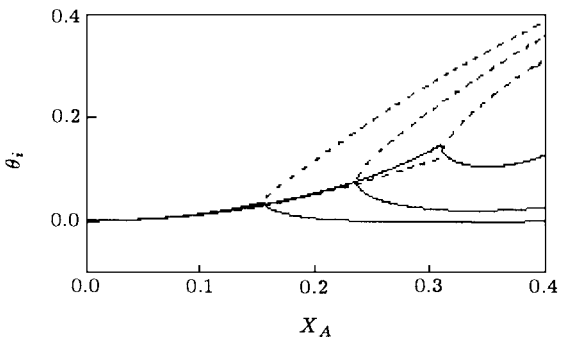


Fig.5. θ_A (——) and its decrease $\theta_A[1-(1-\theta_B)^N]$ (- - - - -). These almost identify with each other for $X_A < X_{A1}^C(N)$.

(3) One more interesting behaviour of the low-SRP is that θ_E is nearly a linear function of X_A, that is, $\theta_E = bX_A$. Here b takes a value of about 1.10. Considering that θ_A equals its decrease (as mentioned above) and also its increase under the steady-state condition, one has $\theta_A = bX_A^2$ and $\theta_B = 1 - bX_A - bX_A^2$. These relations may also be seen from Figs.2 or 3, in which both θ_A and θ_B are parabola-shaped in the low-SRP region.

5. Remarks

As seen above, the site-approximation mean-field theory may predict both first-order and second-order phase transitions in a model surface reaction system, once the effects of lattice structure on the transformation probability are taken into account. The low-SRP predicted by the present mean-field approach may be regarded as a 'shadowing' of the B-saturated phase.

In principle, one could build a theory as accurate as possible (see, for example, Ref.[14]), which means a task extremely laboured, if not impracticable. The site-approximation mean-field approach, due to its simplicity in operation and adaptability to different cases, is still widely used to obtain a quick impression of behaviours in a system, or to give a rough explanation of some computer simulation results. The approximation scheme presented in this paper has its merits, compared to the traditional BW approximation, being more accurate in description and having more direct predictive power. In this scheme, a CA model is formulated on a general lattice, and the lattice freedom parameter N enters into the theory as a variable. This allows us to analyse the effect of geometric factors on the kinetics in a model dynamical system, when necessary.

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