PHYSICAL REVIEW E VOLUME 58, NUMBER 1 JULY 1998

Kinetic phase transition of the dimer-dimer surface reaction model

Hou Zhonghuai, Yang Lingfa, and Xin Houwen*
Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui, 230026, People's Republic of China

(Received 12 June 1997; revised manuscript received 29 December 1997)

The dimer-dimer (DD) reaction model $\frac{1}{2}A_2+B_2\rightarrow AB_2$ is studied by means of Monte Carlo simulation and mean field theory based on the law of mass action, site approximation, and pair approximation. We find that both site and pair approximation can well reproduce the phase diagrams of the DD model. This fact implies that correlation effects are not so important in the vicinity of the first-order phase transition characteristic of the DD model. A variant of the DD model, which accounts for the recombination of the intermediate product C, is also studied. We find that $C+C$ reaction does not change the qualitative critical behavior of the DD model. [S1063-651X(98)05207-6]

PACS number(s): 05.40.+j, 05.70.Ln, 82.20.Mj, 82.65.Jv

I. INTRODUCTION

The subject of reaction kinetics and irreversible phase transitions (IPTs) in surface catalysis is of great current interest. Great efforts have been concentrated on studies of particular models such as monomer-monomer (MM) [1–5], dimer-monomer (DM) [6–19], dimer-dimer (DD) [20–22], dimer-monomer-monomer (DMM) [23], dimer-dimer-monomer (DDM) models [23–26], etc. These models are all based on the Langmuir-Hinshelwood (LH) mechanism, i.e., all reactants are adsorbed on the surface, and all exhibit IPTs, which are of first order or of second order, between poisoned (saturated) states and stable reactive states. Inspired by the catalytic oxidation of hydrogen, the DD model $\frac{1}{2}A_2+B_2\rightarrow AB_2$ (here A_2 and B_2 correspond to O_2 and H_2 in real systems, respectively) was recently proposed by Albano. According to the LH mechanism, it is assumed that the reaction occurs according to the following steps:

$$A_2+2S\rightarrow 2A(a), \tag{1a}$$

$$B_2+2S\rightarrow 2B(a), \tag{1b}$$

$$A(a)+B(a)\rightarrow C(a)+S, \tag{1c}$$

$$B(a)+C(a)\rightarrow BC(g)+2S. \tag{1d}$$

Here S denotes an empty surface site, C stands for the intermediate product AB, and (g) and (a) correspond to gaseous or adsorbed species, respectively. For this model, a first-order IPT exists at the stoichiometric value $y_{1B}=\frac{2}{3}$, such that for $y_B>y_{1B}$ $(y_B<y_{1B})$, where y_B is the mole fraction of B_2 in the gas phase, the surface is poisoned (saturated) by B (a binary compound of A and C), respectively.

At lower temperature in real catalytic process, the reaction between C should also be considered [21]:

$$C(a)+C(a)\rightarrow BC(g)+A(a)+S. \tag{1e}$$

A rather counterintuitive result was reported by Albano that $C+C$ reaction leads to a reactive window with two IPTs at $y_{1B}\simeq 0.4525$ and $y_{2B}\simeq 0.6263$. One notes that the reaction between C does not change the stoichiometric ratio between A_2 and B_2, so there cannot be a reactive window. Although the simple mean field analysis proposed by Albano predicted the same qualitative feature, one should note that the roles of A_2 and B_2 are obviously switched in Eqs. (2a) and (2b) in Ref. [21]: the $C+C$ reaction should result in increment of A coverage rather than B coverage. So there may be some trivial error in Ref. [21]. To make clear this point, we have also studied the role of $C+C$ reaction by Monte Carlo simulation (MCS) in the present work. In fact, as expected, $C+C$ reaction does not alter the qualitative critical behavior of the DD model, i.e., still only a first-order IPT exists at $y_{1B}=\frac{2}{3}$. This result is further supported by mean field analysis.

Since Dickman's work on the ZGB model [7], a lot of efforts have been contributed to theoretical analysis of the ZGB model and its variants [7–9,17,19]. It is well known now that mean field theory (MFT) within pair approximation (PA) can well reproduce the phase diagram of the ZGB model, i.e., both the second-order and the first-order IPTs characteristic of the ZGB model are obtained, while site approximation (SA) fails to reproduce the second-order one. This fact indicates that at least pair correlation should be considered to produce the second-order IPT. On the other hand, from Dickman's work, one knows that SA and PA predict the same ‘‘spinodal’’ point, which seems to imply that correlation effects are not so important in the vicinity of the first-order IPT of the ZGB model.

So a straightforward question arises: to what extent should the correlation effects be considered in other surface reaction models, such as the DD model, which is much more complex than the ZGB model? To answer this question, one must study the model by analytical approaches and compare their predictions with MCS results. In fact, Maltz and Albano have done this in Ref. [21]. Nevertheless, the equations of motion there were based on the law of mass action (LMA), the validity of which should be viewed with skepticism in heterogeneous surface reactions such as the DD model, especially when clustering effects are important. In addition, the trivial error in the equations, as mentioned above, should also be corrected. So in the present work, we will apply SA and PA method to the DD model. To provide a comparison, the corrected version of LMA is also presented.

---

*Author to whom correspondence should be addressed.

There is another motivation to perform theoretical analysis on this kind of complex surface reaction models. One knows that MCS often requires a large amount of computer time due to the use of large lattice and averaging over a large number of independent runs. Although in analytical work, one should also perform numerical integration of the equations of motion to obtain the critical values and the phase diagrams, the computer time needed is much shorter. Thus if one can demonstrate the universal validity of an analytical method, e.g., SA or PA, there is a possibility to study the critical behavior of surface reaction models, if one cares more about the qualitative features, in a more convenient way than MCS.

Albano had also considered the roles of B diffusion, B desorption, and C desorption, and a unitary diffusion rate and infinite desorption rates were used in his work. When B desorbs, the critical point shifts to $y_{1B}=0.7014$, and a reactive window occurs for $y_B<y_{1B}<1$. When C desorbs, one finds two critical points at $y_{1B}\simeq 0.56$ and $y_{2B}\simeq 0.649$. In the present work, we will further consider the role of A desorption with finite desorption rate. Our major purpose is to determine if the theoretical analysis remains valid for the variants of the DD model. The present paper is organized as follows: in Sec. II the three types of mean field theory are presented followed by the major results and discussions; in Sec. III we study the role of $C+C$ reaction; and we state our conclusions in Sec. IV.

II. MEAN FIELD THEORY FOR THE DD MODEL

In this section, we would like first to give a brief introduction to the simulation algorithm, which would be helpful in the derivations of the equations of motion. At the beginning, an adjacent pair of empty sites is randomly picked (the trial ends if not successful) and a dimer A_2 (B_2) is adsorbed with probability y_A $(1-y_A)$, respectively. After the adsorption of a dimer, the six neighboring sites are checked for reaction (1c) and (1d). Notice C is formed on a site which is originally occupied by A while the site corresponding to B is vacant. When more than one B is found in the neighborhood of an A, one of them is selected randomly to form a C which immediately reacts with another B to form $BC(g)$. The reaction partners are chosen randomly out of the neighboring sites of a B if they are of the same type, otherwise the reaction between B and C takes precedence over that between B and A. If $C+C$ reaction is considered, the neighborhood of a newly formed C must be checked for possible further reactions. After each adsorption trial, the desorption step of i species $(i=A,B,C)$ is repeated for dp_i times. For more details, one can turn to Albano's paper [21].

Now the mean field treatments can be formulated, based on LMA, SA, or PA, respectively. At the beginning, we would like to consider the original DD model, i.e., the $C+C$ reaction is not included.

According to LMA spatial homogeneity is assumed and all correlations are neglected. The rate equations are written as

$$\frac{d\theta_A}{dt}=2y_AK_A^a\theta_S^2-K_C^f\theta_A\theta_B-2K_A^d\theta_A^2, \tag{2a}$$

$$\frac{d\theta_B}{dt}=2y_BK_B^a\theta_S^2-K_C^f\theta_A\theta_B-K_{BC}^f\theta_B\theta_C-2K_B^d\theta_B^2, \tag{2b}$$

$$\frac{d\theta_C}{dt}=K_C^f\theta_A\theta_B-K_{BC}^f\theta_B\theta_C-K_C^d\theta_C, \tag{2c}$$

$$R_{BC}=K_{BC}^f\theta_B\theta_C. \tag{2d}$$

The superscripts a, d, and f stand for ''adsorption,'' ''desorption,'' and ''formation,'' respectively; θ_i $(i=A,B,C,S)$ denote the average coverage of i species; R_{BC} is the rate of BC production. For this approach, the probability to find an empty pair is θ_S^2. As Albano did, we also choose $K_A^a=K_B^a=K_C^f=K_{BC}^f=1$ and let other rate coefficients vary. One should note that this choice is rather arbitrary, which also limits the validity of LMA: another choice of these constants would lead to different results.

Identical with LMA, SA also neglects all correlations and the probability to find an empty pair is θ_S^2 too. However, it is directly based upon the elementary reaction steps occurring on the lattice, such that it contains no undetermined rate constants and can provide quantitative comparison with MCS. Following the main idea proposed in Dickman's work, one can readily obtain

$$\frac{d\theta_A}{dt}=2y_A\theta_S^2(1-\theta_B)^3-2y_B\theta_S^2[(1-\theta_C)^3-(1-\theta_A-\theta_C)^3]-2K_A^d\theta_A^2, \tag{3a}$$

$$\frac{d\theta_B}{dt}=2y_B\theta_S^2(1-\theta_A-\theta_C)^3-2y_A\theta_S^2[3\theta_B(1-\theta_B)^2+6\theta_B^2(1-\theta_B)+2\theta_B^3]-2K_B^d\theta_b^2, \tag{3b}$$

$$\frac{d\theta_C}{dt}=2y_B\theta_S^2[(1-\theta_C)^3-(1-\theta_A-\theta_C)^3]+6y_A\theta_S^2\theta_B(1-\theta_B)^2-2y_B\theta_S^2[1-(1-\theta_C)^3]-K_C^d\theta_C, \tag{3c}$$

$$R_{BC}=4y_A\theta_S^2[3\theta_B^2(1-\theta_B)+\theta_B^3]+2y_B\theta_S^2[1-(1-\theta_C)^3]. \tag{3d}$$

According to Eq. (3a), A adsorption (the first term) leads to increment of θ_A, given that there is no B species in the three neighboring sites of either of the two newly adsorbed A species; B adsorption and following successful reaction with A, given that there is no C in its neighborhood, decreases θ_A (the second term). The third term in Eq. (3a) stands for A desorption. The terms in Eqs. (3b) and (3c) can be interpreted in a similar way, considering the fact that adsorbed A may react with more than one B.

Differently from LMA and SA, which neglect all correlations, PA takes into account pair correlation. Now one should derive the equations of motion for the pair concentrations x_{ij} (notice the probability to find an empty pair just reads x_{SS} according to PA). However, this is rather tedious work for the DD model due to the complexity of the reaction mechanism and the fact that one must check immediately for reactions after adsorption. One must distinguish between the processes taking place on the surface leading to different pair-change numbers (PCNs) and between different configurations which might lead to a given process. In Table I we show the processes and the corresponding rates R^k, where we use notes and diagrammatic forms for the initial configurations to help illustrate the processes. Processes $(1a)-(1f)$ belong to the A-adsorption group; $(2a)-(2f)$ stand for B-adsorption processes and $(3a)-(3c)$ are desorption steps. According to the standard statistical rules proposed by Dickman, the derivation of the rates is rather straightforward according to the notes. The PCNs ΔN_{ij} are given in Table II. Notice that ΔN_{ij} for each process comes from different possible initial configurations which have different rates and different contributions to ΔN_{ij}, e.g.,

$$\Delta N_{ij}^{(1b)} = \tfrac{1}{3}\Delta N_{ij}(SSB) + \tfrac{2}{3}\Delta N_{ij}\begin{pmatrix} S & S \\ * & B \end{pmatrix}.$$

Now the equations of motion read

$$\frac{dx_{ij}}{dt} = \sum_k \Delta N_{ij}^k R^k, \tag{4a}$$

$$R_{BC} = R^{1d} + R^{1e} + R^{1f} + R^{2d} + R^{2e} + 2R^{2f}. \tag{4b}$$

Performing numerical integration of Eqs. (2a)–(4b), one can readily obtain the critical values and phase diagrams of the DD model, including the effects of desorption of the adsorbed species. The major results are interpreted in Figs. 1 and 2, where the variations of θ_A, θ_B, and θ_C with y_A, obtained from LMA, SA, PA, and MCS are presented. For Fig. 1, all desorption rates are 0, while for Fig. 2, $dp_A = 1$ and $dp_B = dp_C = 0$. It is straightforward to study the roles of B desorption or C desorption by these equations or MCS, but the qualitative results are nothing different from that obtained by Albano and thus it is not necessary to repeat them here.

On first look at Fig. 1, one finds that all the three types of mean field analysis predict a first-order IPT at $y_{1B} = \frac{2}{3}$, in correct agreement with MCS. However, it is clear that SA and PA provide a much better quantitative prediction than LMA. In the vicinity of the IPT, one sees that there is little difference between SA and PA, while away from the IPT, PA is better than SA. For example, PA can well reproduce the ''jam'' effect when $y_A = 1$ or $y_B = 1$, i.e., the total coverage is about 0.88 due to the requirement of empty pairs for dimer adsorption, while SA predicts that the surface is totally poisoned by A or B, respectively.

Looking at Fig. 2, for which A desorption is considered, one also finds that both SA and PA can well reproduce the phase diagrams obtained by MCS. Now the critical point exists at $y_{1A} = 0.345, 0.338, 0.333, 0.332$ according to MCS, PA, SA, and LMA, respectively. A reactive window occurs in the interval $y_{1A} < y_A < 1$. For $y_A = 1$, the coverage of A reads $1/(1 + dp_a) = 0.5$, while a rather small presence of B_2 in the gas phase reduces θ_A to about 0.4 and increases θ_C to 0.2. It is shown that this interesting characteristic can be correctly reproduced by SA and PA, but not LMA.

We now can draw the conclusion that both PA and SA are valid for the DD model which has only one first-order IPT. This fact seems to support the point of view that correlation effects are not so important in the vicinity of a first-order IPT, which was also implied, as mentioned above, by Dickman's work on the ZGB model. So SA may be sufficient to produce first-order IPTs. We will further discuss this point in the next section where $C + C$ reaction is considered.

III. THE ROLE OF $C + C$ REACTION

In this section the role of $C + C$ reaction is studied. As stated in the Introduction, the results reported by Albano were rather counterintuitive—that $C + C$ reaction leads to a reactive window. In fact, after investigation of the equations of motion proposed in Ref. [21], one can find something wrong that A_2 and B_2 are switched. We have performed MCS in the present work and we find that $C + C$ reaction does not change the qualitative critical behavior of the DD model, i.e., the first-order IPT still exists at $y_{1B} = \frac{2}{3}$ and no reactive window appears, as is shown in Fig. 3. This is reasonable because $C + C$ reaction does not change the stoichiometry of the model (notice if C desorbs, the stoichiometric ratio between A_2 and B_2 changes to 1:1 such that another critical point appears as was reported in Albano's work). Compared to the original DD model, θ_A (θ_C) is higher (lower) in the interval $0 < y_B < y_{1B}$, which is obviously due to the fact that $C + C$ forms $BC(g)$ and $A(a)$.

It is also feasible to study the role of $C + C$ reaction by mean field analysis constructed in the preceding section. According to LMA, one just needs to add corresponding terms to Eqs. (2a) and (2c). Hence

$$\Delta \frac{d\theta_C}{dt} = -2\Delta \frac{d\theta_A}{dt} = -2K_{BC}'^{f}\theta_C^2. \tag{5}$$

Here $K_{BC}'^{f}$ is the rate constant of $C + C$ reaction. For SA and PA, however, difficulty arises because one must check immediately the neighborhood of a newly formed C for further possible reactions. According to SA, the equations of motion now change to

$$\frac{d\theta_A}{dt} = 2y_A\theta_S^2\{(1-\theta_B)^3 + 3\theta_B(1-\theta_B)^2[1-(1-\theta_C)^3]\} - 2y_B\theta_S^2[(1-\theta_C)^3 - (1-\theta_A-\theta_C)^3](1-\theta_C)^3, \tag{6a}$$

$$\frac{d\theta_B}{dt} = 2y_B\theta_S^2(1-\theta_A-\theta_C)^3 - 2y_A\theta_S^2[3\theta_B(1-\theta_B)^2 + 6\theta_B^2(1-\theta_B) + 2\theta_B^3], \tag{6b}$$

$$\frac{d\theta_C}{dt} = 2y_B\theta_S^2[(1-\theta_C)^3 - (1-\theta_A-\theta_C)^3][2(1-\theta_C)^3 - 1] + 6y_A\theta_S^2\theta_B(1-\theta_B)^2[2(1-\theta_C)^3 - 1] - 2y_B\theta_S^2[1-(1-\theta_C)^3]. \tag{6c}$$

Here we have not included the desorption terms. For PA, one should further distinguish the processes listed in Table I.

TABLE I. List of adsorption and desorption processes for the DD model and their rates. Notice the $\ast$ in the diagrammatic forms must be of type S.

Process	Diagrams	Rates (R^k)	Notes
$(1a)$	$S\ S$	$(1-b_s)^6 y_a x_{ss}$	Neither S site has NN $B(s)$
$(1b)$	$S\ S\ B$, and $\begin{array}{cc} S & S \\ \ast & B \end{array}$	$6b_s(1-b_s)^5 y_a x_{ss}$	One has only one NN B; the other has none
$(1c)$	$\begin{array}{cc} S & S \\ B & B \end{array}$, and $\begin{array}{ccc} S & S & B \\ B & \ast & \end{array}$	$9b_s^2(1-b_s)^4 y_a x_{ss}$	Both have only one NN B
$(1d)$	$\begin{array}{ccc} B & S & S \\ & B & \ast \end{array}$, and $\begin{array}{cc} B & \ast \\ S & S \\ B & \ast \end{array}$	$[6b_s^2(1-b_s)^4+2b_s^3(1-b_s)^3]y_a x_{ss}$	One has more than NN $B(s)$; the other none
$(1e)$	$\begin{array}{ccc} B & \ast & \\ S & S & B \\ B & \ast & \end{array}$, $\begin{array}{cc} B & \ast \\ S & S \\ B & B \end{array}$, $\begin{array}{cccc} & B & \ast & \\ B & S & S & B \end{array}$, $\begin{array}{ccc} & B & B \\ B & S & S \end{array}$	$[18b_s^3(1-b_s)^3+6b_s^4(1-b_s)^2]y_a x_{ss}$	One has more than two NN $B(s)$, the other only one
$(1f)$	$\begin{array}{cccc} B & S & S & B \\ & B & B & \end{array}$, $\begin{array}{cc} B & B \\ S & S \\ B & B \end{array}$, $\begin{array}{cccc} & B & & \\ B & S & S & B \\ & & B & \end{array}$	$[9b_s^4(1-b_s)^2+6b_s^5(1-b_s)+b_s^6]y_a x_{ss}$	Both have more than two NN $B(s)$
$(2a)$	$S\ S$	$(1-\mu)^6 y_b x_{ss}$	Neither S site has NN $A(s)$ or NN $C(s)$
$(2b)$	$S\ S\ A$, and $\begin{array}{cc} S & S \\ \ast & A \end{array}$	$2(1-\mu)^3[(1-c_s)^3-(1-\mu)^3]y_b x_{ss}$	Neither has NN C; but one has NN $A(s)$
$(2c)$	$\begin{array}{cc} S & S \\ A & A \end{array}$, and $\begin{array}{ccc} S & S & A \\ A & & \end{array}$	$[(1-c_s)^3-(1-\mu)^3]^2 y_b x_{ss}$	Neither has NN C; but both have NN $A(s)$
$(2d)$	$S\ S\ C$, and $\begin{array}{cc} S & S \\ \ast & C \end{array}$	$2(1-\mu)^3[1-(1-c_s)^3]y_b x_{ss}$	One has NN $C(s)$; and no NN $A(s)$ or NN $C(s)$ for the other
$(2e)$	$\begin{array}{cc} S & S \\ C & A \end{array}$, and $\begin{array}{ccc} S & S & A \\ C & & \end{array}$	$2[1-(1-c_s)^3][(1-c_s)^3-(1-\mu)^3]y_b x_{ss}$	One has NN $C(s)$; the other has NN $A(s)$, but no NN $C(s)$
$(2f)$	$\begin{array}{cc} S & S \\ C & C \end{array}$, and $\begin{array}{ccc} S & S & C \\ C & & \end{array}$	$[1-(1-c_s)^3]^2 y_b x_{ss}$	Neither has NN $C(s)$
$(3a)$	$A\ A$	$x_{aa} dp_a$	A_2 desorption
$(3b)$	$B\ B$	$x_{bb} dp_b$	B_2 desorption
$(3c)$	C	$x_c dp_c$	C desorption

where $i_s=\frac{x_{is}}{2x_s}$, and $\mu=a_s+c_s$.

Since it is rather complicated, we just give an example here to illustrate the main idea. For process $(2c)$, the initial configurations

$$\begin{array}{cc} S & S \\ A & A \end{array}$$

and

$$\begin{array}{ccc} S & S & A \\ A & & \end{array}$$

first change to

$$\begin{array}{cc} S & S \\ C & C \end{array}$$

TABLE II. Pair-number changes for the processes listed in Table I.

Process	ΔN_{ss}	ΔN_{as}	ΔN_{bs}	ΔN_{cs}	ΔN_{aa}	ΔN_{bb}	ΔN_{cc}
$(1a)$	$-1-6\beta_{bss}$	$6(\beta_{bss}-\beta_{bas})$	0	$-6\beta_{bcs}$	$1+6\beta_{bas}$	0	0
$(1b)$	$-1+\frac{7}{3}s_b-\frac{13}{3}\beta_{bss}$	$\frac{2}{3}+\frac{7}{3}\beta_{bss}-\frac{13}{3}\beta_{bas}$	$-\frac{5}{3}+\frac{7}{3}(b_b-s_b)$	$1-\frac{13}{3}\beta_{bcs}+2\beta_{bss}$	$\frac{7}{3}\beta_{bas}$	$-\frac{7}{3}b_b$	$2\beta_{bcs}$
$(1c)$	$-\frac{7}{9}+\frac{43}{9}s_b-\frac{29}{9}\beta_{bss}$	$-\frac{29}{9}\beta_{bas}$	$-\frac{25}{9}+\frac{43}{9}(b_b-s_b)$	$\frac{25}{9}+\frac{29}{9}(\beta_{bss}-\beta_{bcs})$	0	$-\frac{2}{9}-\frac{43}{9}b_b$	$1+\frac{29}{9}\beta_{bcs}$
$(1d)$	$1+\frac{14}{3}s_b-\frac{5}{3}\beta_{bss}$	$\frac{7}{3}+\frac{5}{3}(\beta_{bss}-\beta_{bas})$	$\frac{10}{3}+\frac{14}{3}(b_b-s_b)$	$-\frac{5}{3}\beta_{bcs}$	$\frac{5}{3}\beta_{bas}$	$-\frac{14}{3}b_b$	0
$(1e)$	$\frac{13}{9}+\frac{65}{9}s_b-\frac{10}{9}\beta_{bss}$	$-\frac{10}{9}\beta_{bas}$	$-\frac{35}{9}+\frac{65}{9}(b_b-s_b)$	$\frac{26}{9}+\frac{10}{9}(\mathrm{B}_{bss}-\beta_{bcs})$	0	$-\frac{4}{9}-\frac{65}{9}b_b$	$\frac{10}{9}\beta_{bcs}$
$(1f\ )$	$\frac{44}{9}+\frac{92}{9}s_b$	0	$-4+\frac{92}{9}(b_b-s_b)$	0	0	$-\frac{8}{9}-\frac{92}{9}b_b$	0
$(2a)$	$-1-6\beta_{uss}$	0	$6(\beta_{uss}-\beta_{ubs})$	0	0	$1+6\beta_{ubs}$	0
$(2b)$	$-\frac{1}{3}(5+7\beta_{uss})$	$-\frac{1}{3}(5+7s_a)$	$\frac{1}{3}(5+7\beta_{uss}-7b_s)$	$-\frac{1}{3}(5+7s_a)$	$-\frac{7}{3}a_a$	$\frac{7}{3}b_s$	$\frac{7}{3}c_a$
$(2c)$	0	$-2-\frac{50}{9}s_a$	0	$2+\frac{50}{9}s_a$	$-\frac{2}{9}-\frac{50}{9}a_a$	0	$\frac{2}{9}+\frac{50}{9}c_a$
$(2d)$	$\frac{7}{3}(s_c-\beta_{uss})$	$\frac{7}{3}a_c$	$\frac{7}{3}(\beta_{uss}-\beta_{ubs})+\frac{5}{3}$	$\frac{7}{3}(c_c-ssc)-\frac{5}{3}$	0	$\frac{7}{3}\beta_{ubs}$	$-\frac{7}{3}c_c$
$(2e)$	$1+\frac{25}{9}s_c$	$-1+\frac{25}{9}(a_c-s_a)$	0	$\frac{2}{9}+\frac{25}{9}(c_c+s_a-s_c)$	$-\frac{25}{9}a_a$	0	$-\frac{25}{9}(c_a-c_c)$
$(2\ f\ )$	$\frac{20}{9}+\frac{50}{9}s_c$	$\frac{50}{9}a_c$	0	$-2+\frac{50}{9}(c_c-s_c)$	0	0	$-\frac{2}{9}-\frac{50}{9}c_c$
$(3a)$	$1+6s_a$	$6(a_a-s_a)$	0	$6c_a$	$-1-6a_a$	0	0
$(3b)$	$1+6s_b$	0	$6(b_b-s_b)$	0	0	$-1-6b_b$	0
$(3c)$	$4s_c$	$4a_c$	0	$(4c_c-s_c)$	0	0	$-4c_c$

$$\text{where } i_j=\frac{(1+\delta_{ij})x_{ij}}{2x_j} \qquad (i,j=A,B,C \text{ or } S),$$

$$\beta_{bij}=\beta_b(1+\delta_{ij})x_{ij}, \qquad \beta_b=\frac{1}{2x_s-x_{bs}}, \qquad \delta_{ij}=\begin{cases}1 & \text{if } i=j\\ 0 & \text{otherwise.}\end{cases}$$

$$\beta_{uij}=\beta_u(1+\delta_{ij})x_{ij}, \qquad \beta_u=\frac{1}{2x_s-x_{as}-x_{cs}}$$

and

$$\begin{array}{ccc} S & S & C\\ C & & \end{array}$$

after B_2 adsorption, respectively. Immediately,

$$\begin{array}{cc} S & S\\ C & C \end{array}$$

changes to

$$\begin{array}{cc} S & S\\ A & S \end{array}$$

with probability one. According to

$$\begin{array}{ccc} S & S & C\\ C & & \end{array}$$

however, further reactions depend on the nearest neighbors (NN) of the newly formed C. Thus

$$\begin{array}{lccc} & S & S & C\\ (C) & C & & \end{array} \Rightarrow \begin{array}{lccc} & S & S & C\\ (A) & S & & \end{array},$$

with probability

$$2(1-c_a^3)[1-(1-c_a)^3], \quad \text{here } c_a=\frac{x_{ac}}{2x_a},$$

which indicates that one new C has NN C species; and

$$\begin{array}{lcccc} & S & S & C & (C)\\ (C) & C & & & \end{array} \Rightarrow \begin{array}{lcccc} & S & S & S & (A)\\ (A) & S & & & \end{array},$$

with probability

$$[1-(1-c_a)^3]^2,$$

to denote that both newly formed C have NN C species; and if there is no NN C species for both, the probability of which is $(1-c_a)^6$, then the initial configuration remains unchanging. After these steps, one should work out the PCNs for

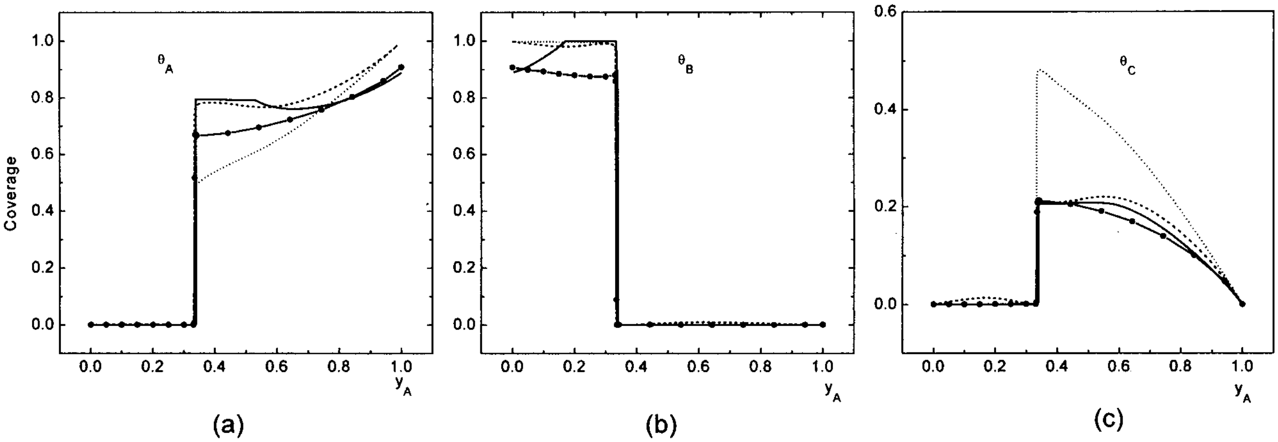

FIG. 1. Variations of (a) θ_A, (b) θ_B, (c) θ_C with y_A for the original DD model obtained by MCS (circles); PA (solid line); SA (dashed line); LMA (dotted line).

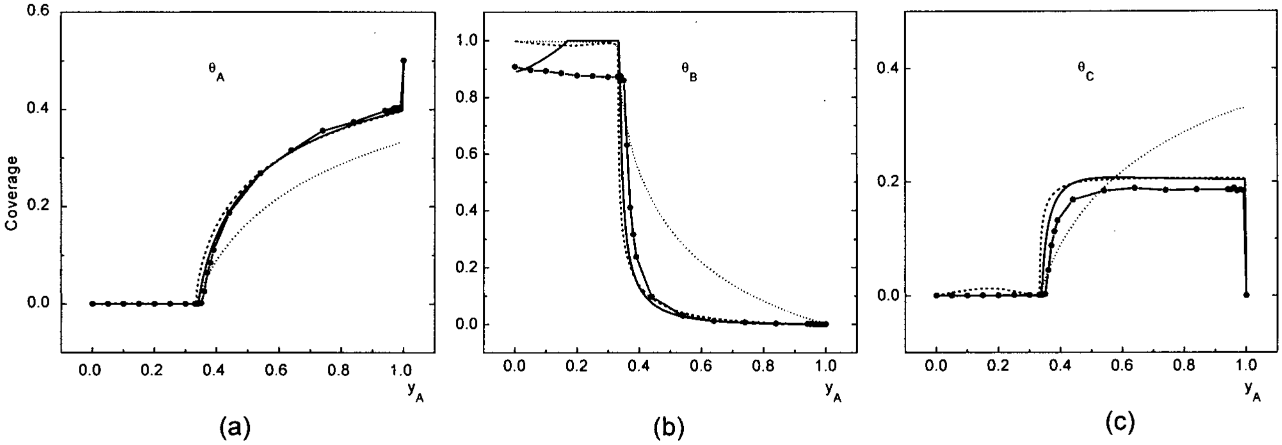

FIG. 2. Variations of (a) θ_A, (b) θ_B, (c) θ_C with y_A for the DD model with A desorption $(dp_A = 1)$ obtained by MCS (circles); PA (solid line); SA (dashed line); LMA (dotted line).

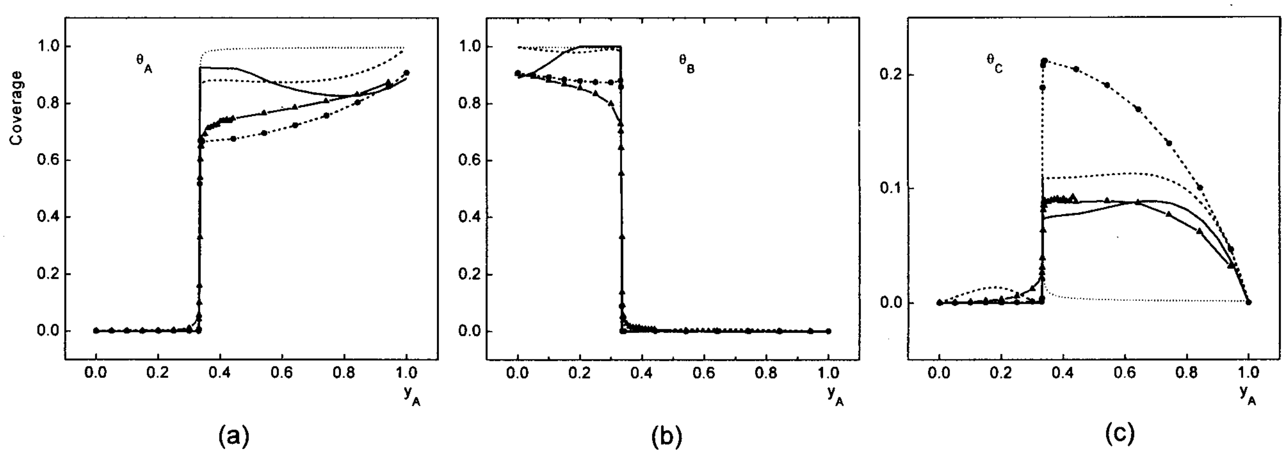

FIG. 3. Variations of (a) θ_A, (b) θ_B, (c) θ_C with y_A for the DD model with $C+C$ reaction obtained by MCS (triangles); PA (solid line); SA (dashed line); LMA (dotted line). The MCS results for the original DD model (circles) are presented for comparison.

these subprocesses. For the sake of simplicity, we do not list the PCNs in the present paper.

The phase diagrams obtained by LMA, SA, and PA are also presented in Fig. 3. The validity of SA and PA is again demonstrated, while LMA is quantitatively bad. In addition, the good agreement between SA and PA further supported the point proposed in the preceding section that correlation effects are not so important in the vicinity of the first-order IPT such that SA is sufficient to produce it.

We would like to note here that if the $C+C$ reaction is realized in a separate simulation step, then one need not check for reaction immediately upon $C(a)$ formation such that the derivation of equations of motion would be highly simplified. That is, one just needs to add corresponding terms into Eqs. (3) and (4). Of course, this would lead to another model.

IV. CONCLUSION

In the present work we have studied a complex surface reaction model, the dimer-dimer model $\frac{1}{2}A_2+B_2\rightarrow AB_2$, by means of Monte Carlo simulation and mean field heory based upon the law of mass action, site approximation, and pair approximation, respectively. One finds that both SA and PA can correctly reproduce the phase diagram of the DD model, especially in the vicinity of the single first-order IPT. Based on this fact, one can draw the conclusion that correlation effects are not important near first-order IPTs, as already implied in Dickman's work. Since simple mean field analysis based on LMA often cannot provide quantitative comparisons with MCS due to the arbitrary choice of rate constants and PA is rather complicated if the reaction mechanism is complex, maybe SA can provide a simple and sufficient approach to reproduce first-order IPTs of surface reaction models. Nevertheless, it is expected that PA can provide more correct quantitative predictions and SA may lose validity to produce second-order IPTs.

We have also studied a variant of the DD model, which takes into account $C+C$ reaction. We find that $C+C$ reaction does not alter the qualitative critical behavior of the model, which is rather comprehensible due to the fact that $C+C$ reaction does not change the stoichiometric ratio between A_2 and B_2. This result is well supported by mean field analysis. In addition, both SA and PA can well reproduce the phase diagram, which further supports the main conclusion of the present work.

ACKNOWLEDGMENT

This work is supported by the National Science Foundation of China and National Laboratory of Theoretical and Computational Chemistry of China.

[1] Robert M. Ziff and Kristen Fichthorn, Phys. Rev. B **34**, 2038 (1986).

[2] A. Sadiq and Khawaja Yaldaram, J. Phys. A **21**, L207 (1988).

[3] K. Fichthorn, E. Gulari, and R. M. Ziff, Phys. Rev. Lett. **63**, 1527 (1989).

[4] K. Fichthorn, E. Gulari, and R. M. Ziff, Chem. Eng. Sci. **44**, 1403 (1989).

[5] D. ben Avraham *et al.*, J. Phys. A **23**, 4297 (1990).

[6] R. M. Ziff, E. Gulari, and Y. Barshad, Phys. Rev. Lett. **56**, 2553 (1986).

[7] Ronald Dickman, Phys. Rev. A **34**, 4246 (1986).

[8] Iwan Jensen and Hans C. Fogedby, Phys. Rev. A **42**, 1969 (1990).

[9] Ronald Dickman, Iwan Jensen, and Hans C. Fogedby, Phys. Rev. A **41**, 3411 (1990).

[10] E. V. Albano, Phys. Rev. B **42**, 10 818 (1990).

[11] E. V. Albano, J. Phys. A **23**, L545 (1990).

[12] E. V. Albano, Surf. Sci. **235**, 351 (1990).

[13] Benjamin J. Brosilow and Robert M. Ziff, Phys. Rev. A **46**, 4534 (1992).

[14] Robert M. Ziff and Benjamin J. Brosilow, Phys. Rev. A **46**, 4630 (1992).

[15] E. V. Albano, Phys. Lett. A **168**, 55 (1992).

[16] J. Satulovsky and E. V. Albano, J. Chem. Phys. **97**, 9440 (1992).

[17] J. W. Evans, J. Chem. Phys. **98**, 2463 (1993).

[18] J. Mai, A. Casties, and W. Von Niessen, Chem. Phys. Lett. **211**, 197 (1993).

[19] Hou Zhonghuai, Yang Lingfa, and Xin Houwen, Surf. Sci. (to be published).

[20] Ezequiel V. Albano, J. Stat. Phys. **69**, 643 (1992).

[21] Alberto Maltz and E. V. Albano, Surf. Sci. **277**, 414 (1992).

[22] E. V. Albano, J. Phys. A **25**, 2557 (1992).

[23] Ezequiel V. Albano, J. Phys. A **29**, 3317 (1996).

[24] Ezequiel V. Albano, Surf. Sci. **306**, 240 (1994).

[25] E. V. Albano, J. Phys. A **27**, 3751 (1994).

[26] E. V. Albano, J. Phys. A **214**, 426 (1995).