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# The effect of phase transitions, surface diffusion, and defects on heterogeneous reactions: multiplicities and fluctuations *

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The influence of attractive absorbate–absorbate interactions and surface diffusion on phase transitions in unimolecular surface reactions is examined by Monte Carlo simulations. Detailed studies in parameter space are performed assuming various forms of desorption and reaction rate expressions. Introduction of rate anomalies can lead either to a kinetic or to an equilibrium phase transition, depending on the reaction kinetics and the rate-determining proce ss. It is demonstrated that migration affects the reaction rate, nucleation, and phase transitions, and, therefore, detailed study of them at a molecular level is necessary to describe heterogeneous reactions. Hysteresis in reactant coverage and reaction rate are studied and large fluctuations are found to dominate the system dynamics near cusp points. The influence of defects which act as nucleation centers on metastability is also investigated. The Monte Carlo data are compared with the predictions of mean-field theory, and limitations of the latter are discussed.

## 1. Introduction

Surface reaction systems frequently exhibit complicated dynamical behavior [1-7]: reaction rate multiplicities, rate oscillations, phase transitions, etc. These non-equilibrium systems are outside of classical statistical mechanics, and no rigorous theories exist to describe them [6,7]. A classical approach for the study of catalytic processes is to use the mean-field approximation (MFA) by writing a system of ordinary differential equations in which a uniform concentration of species over the surface is assumed [1,2,8-11]. However, the MFA cannot handle correctly the formation of islands formed on catalyst surfaces [12,13]. In addition, surface migration is inherently excluded from the model since atoms are assumed uniformly distributed and no concentration gradients exist. Generalization of Fick's Second Law to account for adsorption, desorption,

and reaction with appropriate boundary conditions cannot predict uphill diffusion observed in these situations [14]. As a consequence, MF models, aside from being in many cases analytically intractable because of their complexity, cannot explain the observations of enhanced operation under periodic conditions or the causes of synchronization of multiple oscillators on the catalyst surface to produce global oscillations [4,15,16].

Monte Carlo (MC) simulations [17] can treat processes occurring on the surface taking into account the spatial inhomogeneities and local fluctuations of concentrations. Recently, Ziff, Gulari, and Barshad proposed a MC model (hereafter called ZGB model) to study a bimolecular reaction between a diatomic molecule $A_2$ (representing $O_2$) and a non-dissociative molecule B (representing CO) [6]. In addition, a bimolecular reaction between an atom A and an atom B (hereafter called AB model) has been studied [18]. Subsequently, extensions of the ZGB model and comparison with the MF theory have been described by many groups [5,19-24]. Even though these models simplify the experimental situations, they provide insight into irreversible phase transitions for conditions far from equilibrium.

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In this work, the MC method is used to examine unimolecular catalyzed reactions because more thorough investigation in parameter space is possible compared with bimolecular reactions [10,25]. Furthermore, we suggest that surface unimolecular reactions involve many features which are present in real bimolecular systems. For example, if $\theta$ is the surface coverage, the $(1 - \theta)$ term used here can be a simplified representation of the coverage of a second species with competitive adsorption, i.e. a site not occupied by a reactant can be vacant or blocked by a second species.

Recently, we used the MC method to investigate the problem of kinetic oscillations for a unimolecular reaction in a continuous stirred tank reactor [7]. In this paper, the phenomenon of metastability for conditions close to equilibrium and the phase transition caused by reaction vacant sites are studied for a unimolecular reaction in a constant pressure reactor. Since surface diffusion cannot be modeled by a MF model but it is the dominant process in many experiments, its effect on phase transitions and nucleation is considered.

It is observed experimentally that all surfaces contain defect sites such as dislocations, steps, vacancies, etc. Consequently, the binding energy of atoms to the substrate is not necessarily constant over all the surface [26]. At present, no clear picture of the influence of defects or impurities on global oscillations exists [18,27]. In the study of a continuous-flow reactor, we have shown that defects might strongly affect the existence of kinetic oscillations [7] through the influence on phase transitions. Therefore, their role on the dynamics of heterogeneous reactions, which is absent from the MF model, must be appropriately examined. In this paper, we calculate the isotherms on imperfect surfaces and investigate how defects affect nucleation, metastability, and the location of the transition point.

## 2. Models

### 2.1. Mean field model

In the MFA, the adatoms are assumed uniformly distributed on the surface. In an isother-

mal, mixed reactor, the overall adsorption-desorption–reaction process is described by [10]

$$\frac{d\theta}{dt} = r_a - r_d - r_R, \tag{1}$$

where $r_a$, $r_d$, $r_R$ are the adsorption, desorption, and reaction rates, and $\theta$ is the surface coverage, i.e. the number of atoms adsorbed on the surface divided by the number of surface sites. The gas phase reactant partial pressure $P$ is assumed to be uniform over the surface and constant in time (a differential reactor).

In the presence of absorbate attractive interactions of strength $w (w > 0)$, the change of reactant coverage with time is given in MFA by

$$\frac{d\theta}{dt} = m_a k_a P (1 - \theta)^{m_a}$$
$$- m_a k_{d0} \exp(-z_s \theta w / kT) \theta^{m_a}$$
$$- k_R \theta (1 - \theta)^{m_R}, \tag{2}$$

where $m_a$ is either one or two for first- or second-order kinetics in desorption, $z_s$ is the surface coordination number, and $m_R$ is the number of vacant sites required for reaction. $m_a k_{d0} \theta^{m_a}$ is the desorption rate in the low-coverage limit, $k_R$ is the reaction rate constant, and $k_a$ is the adsorption rate constant over the density of surface sites, $n_0$. For ideal gas kinetics $k_a$ is

$$k_a = \frac{n_0^{-1} s}{(2\pi mkT)^{1/2}}, \tag{3}$$

where $s$ is the sticking coefficient, $m$ is the mass of an atom, $k$ is the Boltzmann constant, and $T$ is the temperature.

According to the MFA, each atom sees a mean field, an average number of nearest neighbors equal to $z_s \theta$. A factor of the form $\exp(-z_s \theta w / kT)$ in the reaction rate of eq. (2) appears to be equivalent to the same factor in the desorption rate which is examined in sections 3–7. However, this term would couple differently with the gas pressure equation in the modeling of a flow reactor [7,10], and this case does not exhibit oscillations [10]. Therefore, in the calculations of a constant pressure reactor presented here, the reaction activation energy is taken to be coverage indepen-

dent. The nonlinear terms in desorption and reaction rates of eq. (2) express the reduction of efficiency in adatom removal caused either by attractive interactions or vacant sites required for example by a large organic molecule to the decompose into products. In reality, these nonlinearities can act independently or simultaneously. In most of our calculations, the reaction rate is taken to be proportional to the reactant coverage ($r_R = k_R\theta$). During growth of clusters, the desorption rate can be reduced by a few orders of magnitude (depending on $w/kT$) compared with the reaction rate which increases with coverage. Hence, the importance of the two processes in removal of atoms during the transient path of the system can vary considerably.

If $m_a = 1$, $m_R = 0$, and $w/kT = 0$, these kinetics are called Langmuir kinetics and the MF model is exact. However, inclusion of absorbate–absorbate interactions or vacant site requirements for either adsorption or reaction can cause deviations from Langmuir kinetics, and in these situations the MF model is not exact. In the following sections, the nonlinear terms in desorption and reaction rates are examined and comparison of the MF model with the MC calculations is presented.

## 2.2. Monte Carlo model

The surface is modeled as a two-dimensional square lattice with periodic boundary conditions. Each time a site is randomly chosen. If this site is empty, adsorption is attempted with probability $p_a$. If the site is occupied, the atom can either desorb, react, migrate with probabilities $p_d$, $p_R$, and $p_m$ respectively, or not move. To choose between these events, a segment proportional to the probability of each process is taken and a random number is used to select which event will be executed. To perform the stochastic simulation, one has to describe the local coverage dependence of the probabilities of the various processes.

The basic steps in the heterogeneous catalysis of unimolecular reactions consist of adsorption of the reactant on the surface, desorption of the reactant and of the product(s) of the reaction, and the reaction step (a Langmuir–Hinshelwood pro-

cess). Adsorption of the reactant A is assumed to occur by chemisorption to a vacant site S

$$A + S \rightarrow AS, \tag{4}$$

where AS denotes the adsorbed species. Each time an atom finds an empty site it adsorbs with probability $p_a$ which is proportional to its gas partial pressure $P$, $p_a \propto k_a P$.

Desorption of reactant A can occur back to the gas phase with probability proportional to the desorption rate

$$AS \rightarrow A + S, \tag{5}$$
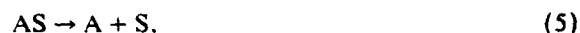
liberating one vacant site. With attractive interactions between the atoms, the activation energy for desorption is coverage dependent and the probability for desorption is

$$p_{d,i} \propto k_{d0} \exp\left(-\sum_j w_j c_j / kT\right), \tag{6}$$

where $w_j$ is the magnitude of interaction between an atom on site $i$ and its $j$th neighbor and $c_j$ is the value of the occupation function at site $j$ which is either zero if the site is empty or one if the site is occupied. The reactant coverage, $\theta$, is the the average value of the occupation function over all the surface

$$\theta = \frac{1}{N_s} \sum_{j=1}^{N_s} c_j. \tag{7}$$

where $N_s$ is the number of surface sites. If the atoms are uniformly distributed, i.e. the value of the occupation function is constant over all the surface, the desorption probability described by eq. (6) coincides with that given by the MF model in eq. (2). Here, we shall only consider first nearest neighbor interactions of strength $w$.

The rate of desorption, $r_d$, is calculated in monolayers per unit time $t$

$$r_d = k_{d0} \frac{d(N_d/N_s)}{dt}. \tag{8}$$

where $N_d$ is the number of atoms desorbed at time $t$.

Reaction of adsorbed species A to produce product B occurs with probability proportional to the reaction rate constant $k_R$

$$AS \rightarrow B + S. \tag{9}$$

The product(s) B formed is assumed to desorb instantly and not interact further with the system. If two vacant sites ($m_R = 2$ in the MFA) are required for deposition of the reaction products of a polyatomic molecule A, i.e.

$$AS + 2S \rightarrow B + 3S \tag{10}$$

then the probability for reaction of an atom on site $i$ is

$$p_{R,i} \propto k_n (1 - c_j)(1 - c_k), \tag{11}$$

where $c_j$, $c_k$ are the values of the occupation function at nearest neighbor sites $j$ and $k$. Sites $j$ and $k$ are randomly chosen. Thus the average probability for reaction is proportional to $k_R$, $k_R/2$, and $k_R/6$ if there are 4, 3, and 2 empty nearest neighbors respectively. Similarly, for the case of one vacant site requirement, only one nearest neighbor site is randomly checked to determine the value of its occupation function.

In the MC simulation the reaction rate is calculated from the number of atoms produced, $N_B$, i.e.

$$r_R = k_R \frac{d(N_B/N_s)}{dt}. \tag{12}$$

In our model, surface diffusion to one of the four nearest-neighbor surface sites is also allowed, invoking the principle of microscopic reversibility or detailed balance [28,29] for each diffusion jump. In general, the dynamics of thermally excited phenomena cannot be described by Kawasaki dynamics or Metropolis walk in which the hopping probability depends only on the energy difference between the final and the initial state of the system [29]. Actually, the migration probability would depend on the energy barrier for an atom to hop [29]. Following Gilmer and Bennema [28], the migration rate, $p_{m,i}$, of an atom on site $i$ jumping to site $j$ is

$$p_{m,i} \propto p_{d,i} \left[\frac{x_s}{a}\right]^2 (1 - c_j), \tag{13}$$

where $x_s$ is the mean displacement of an isolated atom during its time life on the substrate and $x_s/a$ is the average number of jumps executed by an atom on the surface before it desorbs. In this model, the energy barrier depends only on the

local environment of site $i$ [28,30] through $p_{d,i}$, eq. (6).

Most of the simulations have been performed for a $30 \times 30$ surface since size effect analysis indicated no appreciable effect if the lattice size was greater or equal than the one used. Simulations were run on DEC, Apollo, Sparc workstations, and the Cray supercomputers of the Minnesota Supercomputer Institute. Close to a transition point, a typical run of $10^8$ attempts with a program including adsorption, desorption, reaction, and diffusion requires approximately 30–45 minutes of Cray CPU time (without vectorization) and 8–10 CPU hours on an Apollo DN4500.

## 2.3. Real time and Monte Carlo trials

Every attempted event corresponds to a Monte Carlo trial (MCT). Null trials are also allowed in the model. One Monte Carlo step or sweep (MCS) consists of $N_s$ MCT, i.e. it is the time required to sample each surface site once on average. MCS is the usual reported units of time in the literature [6,18]. To compare the MC data with experimental results, the relationship between real time and MCT is required. This is accomplished using the adsorption process [31] since no interactions have to be calculated over all the surface at each moment. If all vacant sites for adsorption were considered to be equivalent, then the average probability per unit time for adsorption on the surface is

$$p_{a,av} = \frac{1}{N_s} \sum_{i=1}^{N_s} k_a P(1 - c_i) = k_a P(1 - \theta). \tag{14}$$

Each time a successful adsorption event occurs, the time elapsed $\Delta t$ corresponds to the average adsorption time per site, i.e.

$$\Delta t = \frac{1}{p_{a,av} N_s} = \frac{\tau_a}{(1 - \theta)N_s}. \tag{15}$$

where $\tau_a = 1/k_a P$ is the adsorption time on a clean surface. Since the time elapsed between adsorption events is random [32], the time step is then

$$\Delta t = - \frac{\tau_a}{(1 - \theta)N_s} \ln(\xi), \tag{16}$$

where $\xi$ is a random number between 0 and 1.

The total elapsed time for the simulation is computed from

$$t = \sum_i \Delta t_i. \tag{17}$$

where $i$ runs over all time steps. When the MF model is exact. calculation of the time elapsed to reach a certain coverage indicates agreement between the two models [33].

## 3. Phase transitions and metastability without reaction

In two-dimensions. the MF theory is qualitatively correct in predicting a coverage multiplicity (three solutions) for $w/kT > 1$ in the limit of no reaction. as shown in fig. 1a for $w/kT = 2$. However, this critical value of temperature (above which multiplicity is observed) is overestimated and the exact value at the transition point is known to be 1.76 [17,34]. In the MF theory two of the three solutions are stable (S) and. once the system is in one of them. it will remain in it for an infinite time. An improvement over the MF theory is accomplished by considering pairs of sites on the surface with first nearest neighbor interactions between adatoms instead of uniformly distributed atoms. The isotherm obtained [35], shown also in fig. 1a. is called Fowler–Guggenheim (FG) and is given by

$$KP = \frac{\theta}{1 - \theta}\left[\frac{b - 1 + 2\theta}{2\theta}\right]^{z_s} \exp(-z_s w/kT),$$
$$\tag{18}$$

where $K$ is the adsorption–desorption equilibrium constant. $K \equiv k_a/k_{d0}$, and $b$ is defined as

$$b \equiv \left\{1 + 4\theta(1 - \theta)\left[\exp(w/kT) - 1)\right]\right\}^{1/2}. \tag{19}$$

The characteristics of the FG isotherm concerning multiplicity and stability of the solutions are the same with those of the MF isotherm. However. the agreement with the MC data is considerably improved. The multiplicity regime is large for the MF model and small for the MC method with the FG in between.

The MC method indicates an abrupt (first-order) transition [17] from a low to a high cover-

age as the reactant pressure rises. fig. 1a. Fig. 1b shows a typical plot of the reactant coverage versus time obtained by the MC method starting either
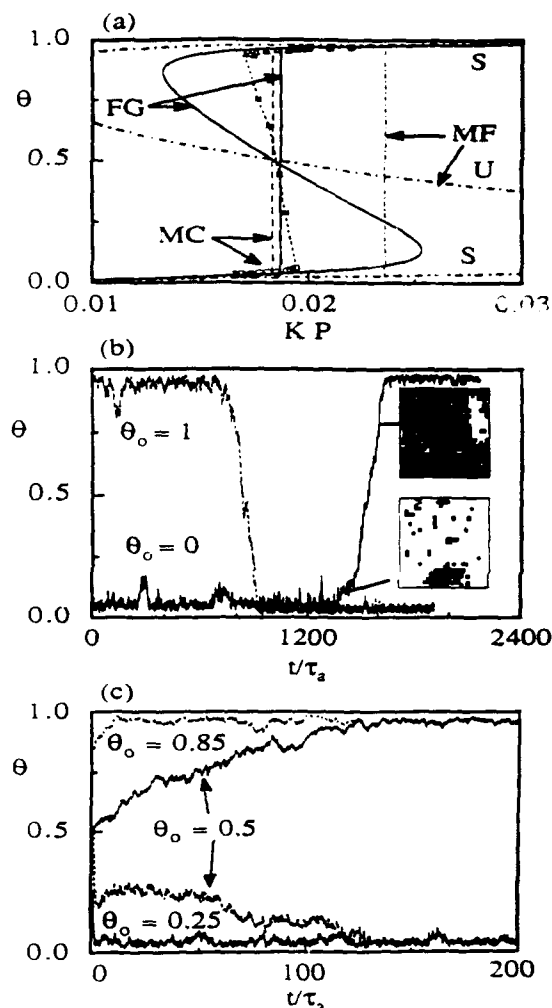


Fig. 1. Panel (a) shows the FG isotherm. the MF isotherm. and the MC data. along with their corresponding tie lines. Metastable states are indicated in panel (b) which shows typical reactant coverage time series. starting from a clean ($\theta_0 = 0$. $KP = 0.0195$) or a totally covered surface ($\theta_0 = 1$. $KP = 0.0172$). and snapshots during nuclei growth. Peaks in the time series which are observed before the transition correspond to growth ($\theta_0 = 0$) or shrinking ($\theta_0 = 1$) of nuclei which subsequently shrink or grow. Panel (c) shows the reactant coverage as a function of time for various values of initial coverage, $\theta_0$ and $KP \approx 0.0186$. Initially. the atoms are randomly deposited on the surface except for the case $\theta_0 = 0.5$ where the atoms are either randomly distributed ($\theta$ decreases with time) or in a stripe ($\theta$ rises with time). The parameters used are $w/kT = 2$. $k_R = 0$. $m_a = 1$.

from a clean surface ($\theta_0 = 0$) or a totally filled surface ($\theta_0 = 1$) where $\theta_0$ is the initial reactant coverage. This figure indicates that without reaction metastable states [31] are found in which the system is trapped for a relatively long time before it can overcome the activation barrier to reach the stable equilibrium state. As the reactant pressure increases, the transition of the system from the metastable state (low coverage) to the stable state (high coverage) occurs in shorter time. At the equilibrium pressure, the lifetime of the metastable state is infinite [17]. Starting from a high partial pressure and decreasing the reactant pressure, hysteresis loop is formed, fig. 1a. Hence coverage multiplicity is found by MC simulations for an isothermal system.

The discontinuous transition from a low to a high coverage is caused by cluster formation and growth due to attractive absorbate–absorbate interactions. Small clusters are formed by local variation in the adsorption of the incoming species and they lower the system free energy. These islands grow and shrink until a critical cluster is formed. Then the probability of this cluster to grow is on the average 50%. A supercritical cluster [36] is formed when one more atom is added to the critical one. As the reactant pressure increases, the size of the biggest cluster increases and when one or more supercritical clusters are formed on the surface, they grow on the average and merge to big clusters covering almost the entire surface. Thus a large enough perturbation due to cluster formation can drive the system from the metastable to its true equilibrium state. Snapshots of the surface configuration when the clusters begin to grow and merge are shown in the inset of fig. 1b. Since the transition found is an equilibrium one, this transition is hereafter called equilibrium transition. The effect of initial conditions, migration, reaction rate expression, and defects on the metastability are now discussed.

### 3.1. Dependence on initial conditions

Outside the multiplicity regime, a unique solution of global minimum free energy is obtained which is independent of the initial surface coverage. However, in the reactant pressure regime

where two states with minima in the energy exist, the state reached by the system during the computational time depends on the initial conditions. According to the MF theory for coverage below the unsteady branch (U), the low-coverage solution is obtained and for initial coverage above the unsteady line, the high-coverage solution is found. However, in the MC simulations, since the distribution of atoms is not uniform due to attractive interactions, the final state approached by the system during the computational time depends not only on the value of the initial coverage, $\theta_0$, but also on the distribution of atoms, fig. 1c. In the MF or FG approximation, the tie lines shown in fig. 1a, can be obtained by the Maxwell equal area rule [10]. However, in practice the unsteady steady branch is not known. At the equilibrium pressure, both states are stable, i.e. the depth of the minima in the free energy of the system are equal.

Because both states are equally accessible, one can start with two equal stripes, one filled and one empty [6], and monitor the time evolution of the system until the surface is either filled or almost empty. Performing 30 individual runs, the equilibrium pressure for which the probability of going up or down is one half was found to be $0.0183 \pm 0.0001$ for $w/kT = 2$. For the values of reactant pressure 0.0182 and 0.0184 the probabilities of going up are 30% and 70% respectively. The same simulations were repeated by locating initially a square cluster at the center of the surface. No effect of the shape of the cluster on the value of the equilibrium pressure has been found. The MC points connected by the dashed line in fig. 1a correspond to one-half probability of going up or down starting with half the surface covered in a stripe.

### 4. Effect of diffusion on metastability

Surface migration is another driving force for nucleus formation and growth because single atoms, executing many jumps on the surface before they desorb (large $x_s/a$) have a large probability during their random walk to be trapped in a cluster. Atoms in the interior of a cluster are not
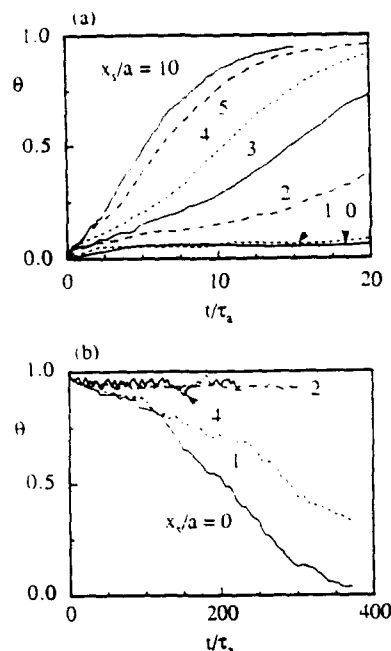
Fig. 2. Effect of surface diffusion on the dynamics of the equilibrium phase transition for a slow reaction ($m_R = 2$, $k_R / k_{d0} = 10^{-3}$) as a function of the average number of jumps, $x_v/a$. Panel (a) corresponds to $\theta_0 = 0$, $KP = 0.02$ and panel (b) to $\theta_0 = 1$, $KP = 0.0168$. Surface diffusion draws the system faster from a low to a high coverage in the presence of attractive interactions.

allowed to jump to neighbor positions, unless there is a hole adjacent to them. Furthermore, atoms at the border of clusters must break all bonds with their nearest neighbors to overcome the migration barrier and diffuse. The more compact is the cluster, the fewer atoms can escape from it. Thus as time proceeds, larger clusters are formed on the surface. Therefore, migration facilitates nucleation and brings the system faster to its stable state, as shown in fig. 2a. Each curve is an average over five individual runs.

In contrast to the transition from a low to a high coverage, if one starts with an initially covered surface, at a sufficiently low reactant pressure, desorption will create holes and disintegrate the surface into small clusters. Hence, desorption competes with diffusion which brings atoms to the clusters and the simulations indicate that diffusion

results in a slowing down of the transition from a high to a low coverage, as shown in fig. 2b.

Therefore, surface migration speeds up the transition from a low to a high coverage but slows down the transition from a high to a low coverage.

## 5. Effect of reaction rate expression on the phase transition

In section 3, the phase transition was examined for the adsorption–desorption process. In this section, the effect of reaction on the phase transition driven by attractive interactions is discussed. The reaction rate is given by $r_R = k_R \theta (1 - \theta)^{m_R}$, where $m_R$ is the number of vacant sites required for decomposition of a polyatomic molecule A. The factor $(1 - \theta)$ can be also considered as the coverage of a second species in a bimolecular reaction. In the following, the cases of zero, one, and two vacant sites are investigated.

### 5.1. Langmuir reaction ($m_R = 0$)

In the interior of clusters, the probability of an atom to desorb is very small due to the large number of bonds it has to break with nearest neighbors. Under these circumstances, the surface reaction can be the dominant mechanism which removes atoms from the interior of nuclei, creating holes and inhibiting nucleation. If the reaction rate constant is not very large, the transition from a low to a high coverage and reaction rate remains abrupt, as shown in fig. 3a. However, since clustering is reduced by the surface reaction, a higher reactant pressure is required for nucleation to occur and therefore the transition is shifted to a higher pressure as $k_R$ is increased. When the reaction rate constant is sufficiently large, nucleation and subsequent growth of clusters is blocked and a smooth isotherm is obtained, as shown in fig. 3a. Starting from a totally covered surface (high reactant pressure) and decreasing the pressure, hysteresis loop is formed, fig. 3a, and therefore, reactant concentration multiplicity and reaction rate multiplicity are observed. In fig. 3, vertical lines depict a discontinuous transition and arrows show the direction of transition (from a

low to a high coverage or vice versa). Hysteresis loop is indicated, whenever it exists, by a pair of lines of the same symbol.

The reduction of the metastable regime as $k_R$ increases is shown in fig. 3c in which the pressure $P_t$ at the two turning points of the S-shaped isotherms is plotted as a function of reaction rate constant, $k_R$. A discontinuous transition is also observed for the average number of nearest neighbors, the percolation order parameter, and

the average size of clusters formed on the surface [33].

The reaction rate (not shown) calculated in the MC simulations is found to be proportional to the reactant coverage, i.e. $r_R/k_R = \theta$, within statistical errors as is predicted by the MF theory. According to the MFA, the desorption rate, $r_d/k_{d0} = \theta \exp(-z_s\theta w/kT)$, plotted as a function of coverage should be independent of $k_R$. However, deviations from the MFA are observed in the desorp-
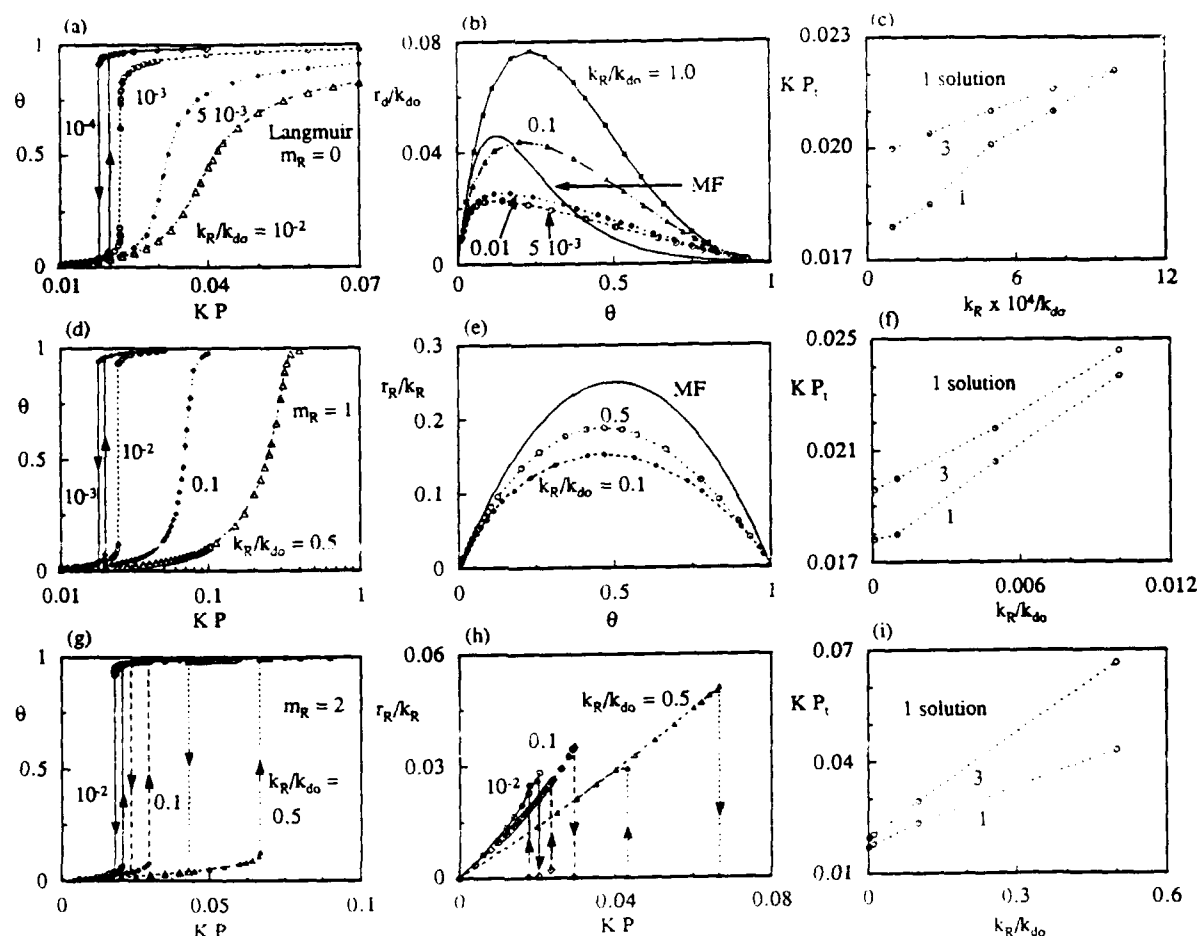


Fig. 3. Effect of reaction rate expression and reaction rate constant, $k_R$, on metastability for $w \cdot kT = 2$. Panels (a)–(c) correspond to $m_R = 0$, (d)–(f) to $m_R = 1$, and (g)–(i) to $m_R = 2$. Lines with the same symbol in panels (a), (d), (g), and (h) show an hysteresis loop in coverage or reaction rate. Panels (a), (d), and (g) show isotherms for the three models. Panel (b) shows deviations from the MFA in desorption rate for the $m_R = 0$ model whereas panel (e) shows deviations from the MFA in reaction rate for the $m_R = 1$ model for various values of $k_R/k_{d0}$. Panel (h) shows hysteresis loops in reaction rate for the $m_R = 2$ model. No single-valued isotherms or rates are obtained for this model. Panels (c), (f), and (i) show the multiplicity regime as a function of $k_R$. No multiple solutions can be found for the $m_R = 0$ and $m_R = 1$ models above a certain value of $k_R$. In contrast the multiplicity regime for the $m_R = 2$ model does not exhibit a cusp point.

tion rate which is not treated correctly because the MF theory does not take into account the formation of clusters on the surface, as shown in fig. 3b. As the reaction rate constant increases, the clusters become less compact and the desorption rate increases. For $k_R/k_{d0} = 1$, it is found that the average number of nearest neighbors seen by an atom does not deviate much from the MF theory. However, large deviations are still observed from the MF desorption rate due to erroneous calculation of the desorption rate based on a uniform surface coverage assumption. Examination of surface configurations and cluster distribution indicates that the reaction creates holes and produces many single atoms in the regime where the maximum of the desorption rate occurs which then increase considerably the desorption rate over the MF estimated value.

### 5.2. One vacant site $(m_R = 1)$ required for reaction

In this case one vacant site is required for the decomposition of molecule A. For small values of the reaction rate constant the transition remains abrupt but the transition point shifts to the right, i.e. to a higher reactant pressure, as shown in fig. 3d. At higher values of the reaction rate constant a smooth isotherm is obtained. Fig. 3f indicates that, as the reaction rate constant increases, the regime in which multiple solutions are observed becomes narrower and a cusp point exists for each value of interaction strength at which the two turning points of the isotherm coincide.

The qualitative behavior of the system is similar to the Langmuir reaction case $(m_R = 0)$ studied above. However, the transition from discontinuous to smooth isotherm occurs at higher reaction rate constant. Since atoms in the interior of compact clusters cannot be annihilated by reaction because they cannot find any vacant site for decomposition, the reaction requiring one vacant site is not as efficient for destroying clusters as the Langmuir reaction examined above. Consequently, multiple solutions exist up to higher reaction rate constants.

When one vacant site is required, both the desorption rate and the reaction rate calculated by the MC simulations deviate from the MFA. As an

example. fig. 3e compares the reaction rate versus reactant coverage for the MFA and the MC model. Based on the MF theory, the reaction rate, $r_R/k_R = \theta(1 - \theta)$, is a parabolic function of $\theta$. Since reaction is considered to be very slow, the formation of clusters is caused mainly by attractive interactions. Nucleation and growth of clusters result in a low reaction probability and thus in a lower reaction rate compared with the case of uniform adatom distribution as shown in fig. 3e. When a discontinuous transition occurs, $r_R/k_R$ is small and corresponds either to a low or to a high coverage (not shown in fig. 3e for reasons of clarity). When a smooth isotherm is obtained, fig. 3d, high reaction rate can be achieved as shown in fig. 3e. The maximum occurs at coverage $\sim 0.5$ in agreement with the MF theory. The higher the reaction rate constant, the higher the randomization of the surface, and the more accurate the MF theory is.

The large deviations of the MC data from the MF can be improved considerably if one considers that the probability of an atom to react is proportional to $(1 - z/4)$, where $z$ is the number of nearest neighbors of that atom. The average reaction rate at steady state can be calculated from the coverage and the average number of nearest neighbors seen by each atom, i.e. $r_R/k_R = \theta(1 - z/4)$. The simulations show very good agreement between the reaction rate calculated that way and the rate obtained by eq. (12). Thus, the failure of the MF theory is due to the wrong averaging over the whole surface which neglects the spatial inhomogeneities, i.e. the cluster formation due to attractive interactions.

### 5.3. Two vacant sites $(m_R = 2)$ required for reaction

In this case two vacant sites are required for the decomposition of the reactant A. Isotherms calculated for different values of the reaction rate constant for $w/kT = 2$ are shown in fig. 3g. As the reaction rate constant increases, more atoms are removed by the chemical reaction and the steady-state value of the reactant coverage decreases. The requirement of two vacant sites is quite restrictive so that atoms have less probability to react compared with the $m_R = 1$ case. Therefore, no appre-
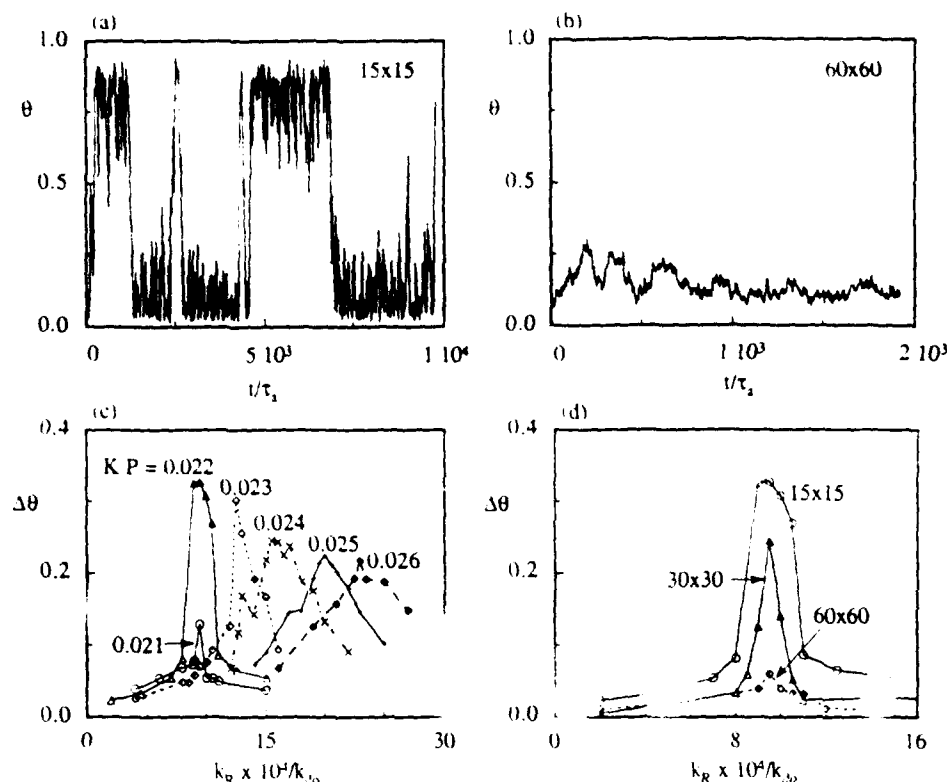
Fig. 4. Dynamics close to the cusp point shown in fig. 1c. Panels (a) and (b) show the fluctuations in reactant coverage versus time for two different lattice sizes. Panel (c) depicts the amplitude of fluctuations, $\Delta\theta$, of a $15 \times 15$ square lattice as a function of reaction rate constant $k_R$, for various values of reactant pressure. Very small fluctuations are found below a certain pressure. Panel (d) shows the amplitude of fluctuations versus $k_R$ at $KP = 0.022$ for three different lattice sizes.

ciable effect of reaction on clustering occurs, and $r_R/k_R$ is only slightly decreased as a result of coverage reduction. Deviations in both the reaction and desorption rates are again observed. Fig. 3h shows hysteresis loops in reaction rate as a function of reactant pressure for various values of the reaction rate constant. No single-valued solution exists for this model.

In contrast with the cases $m_R = 0$ and $m_R = 1$, the discontinuous transition characteristic of the phase transition due to attractive-attractive interactions remains a. o for conditions far for equilibrium. In particular, the multiplicity regime increases with the reaction rate constant, as shown in fig. 3i, i.e. as we leave equilibrium conditions, and no cusp point exists. An abrupt transition from a low coverage (a high reaction rate) to a high coverage (a low reaction rate) is found for all

cases investigated. This phenomenon is caused by the cooperative action of desorption and reaction with vacant sites requirements on cluster formation and will be discussed in more detail in section 8.

## 6. Fluctuations close to a cusp point

The transition from single solution to multiple solutions in coverage and reaction rate is characterized by the existence of a cusp point when $m_R = 0$ or $m_R = 1$. As the reaction rate constant increases, there is a value of the reaction rate constant (depending on the interaction strength) which separates the single solution subspace from the multiple (three) solution subspace. Using the MF theory one can calculate the cusp point rigor-

ously by solving the system of the corresponding equations.

Close to a cusp point, very large fluctuations dominate small areas of the catalyst surface, as shown in fig. 4a for the $m_R = 0$ case. The coverage fluctuates between low and high values. However, this is a size effect as shown in fig. 4b. To analyze the dynamics of the time series obtained by the MC simulations we use the correlation integral method [7,18,37]. We have found [33] that the correlation exponent is proportional to the embedding dimension [7,18,37] as the latter is increased, indicating that the dynamics are dominated by stochastic noise.

To locate a cusp point in a MC simulation for each value of the interaction energy, one has to determine both the reaction rate constant and the gas reactant pressure. First a size effect analysis is used in analogy with the equilibrium Ising model [17]. One can either fix the reaction rate constant and vary the pressure or vice versa, fig. 4c. The maximum of the fluctuations in coverage should indicate the location of the cusp point. Below a certain reactant pressure no large fluctuations are found. This indicates that these simulations are performed in the multiplicity regime where a relatively large perturbation brings the system from one state (a low coverage) to the other (a high coverage). Once the system has left its original state, it does not seem to return to its initial state, at least during the computational time, if its size is large enough. Very large fluctuations are observed when reaction rate constants are slightly greater than the cusp point value, i.e. as we approach the cusp point from the unique solution subspace in agreement with the equilibrium adsorption–desorption system behavior [33]. The dependence of the location of the maximum of fluctuations on the size is not very large as shown in fig. 4d. For the calculations shown in fig. 4, we used a constant number of MCS of approximately 120000 for all sizes of the surface.

The reactant pressure at the turning points of the S-shaped isotherm versus the reaction rate constant is also plotted in fig. 3c. From classical bifurcation theory, one expects that the two turning points (simple folds) will coincide at the cusp point. This is actually observed in fig. 3c, and the

value of pressure and reaction rate constant obtained by this method are in very good agreement with the size effect analysis. Similar dynamic behavior close to the cusp point is also found for the $m_R = 1$ case (not shown).

Our calculations suggest that as a continuation parameter is varied and a cusp point is approached from the smooth isotherm subspace, large fluctuations can determine the dynamics of the system. This is quite analogous with the behavior observed by Fichthorn et al. [18] in their bimolecular AB model where the desorption probability is the bifurcation parameter. In their model, at zero desorption probability a discontinuous isotherm is obtained and as the desorption probability tends to zero a transition from a smooth isotherm to a discontinuous one occurs. However, their model does not have a rigorously defined "cusp point". This difference might explain the fact that their correlation exponent is constant as the embedding dimension increases whereas our correlation exponent is proportional to the embedding dimension.

## 7. Influence of defects on phase transitions

In most of the MC studies a square lattice is used and it was assumed that all sites are equivalent, a highly idealized situation. Experiments indicate that atoms are frequently preferentially adsorbed either at step sites or terrace sites [38,39]. Recently, the influence of surface steps on the phase transitions has been studied by the MC method by examining the size effect dependence of the equilibrium lattice gas model [40].

We restrict our studies to sites with very strong binding energy which are distributed either regularly or randomly on a flat surface (terrace) in the limit of a very slow reaction ($k_R/k_{d0} = 10^{-5}$). It is assumed that atoms on defect sites are very strongly bound on the substrate and they can neither desorb nor react. However, these atoms interact with their first nearest neighbors and constitute nucleation centers. Regularly distributed defects are implemented in the computer as a square cluster at the center of a certain size surface area.
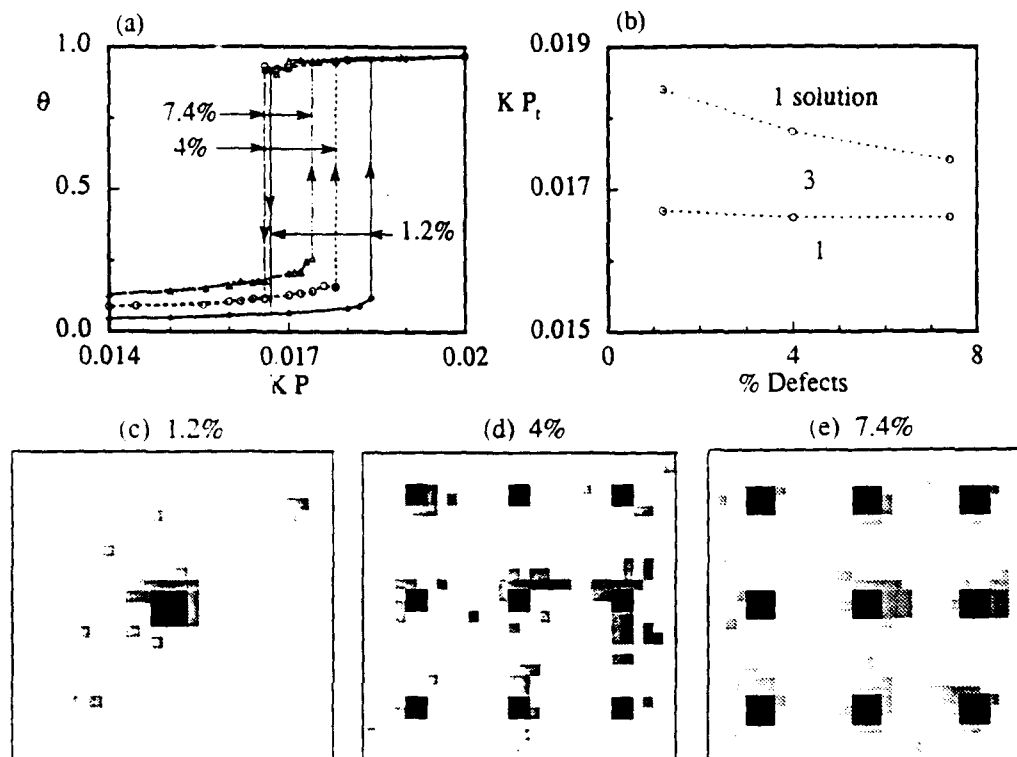
Fig. 5. Influence of concentration of defects on phase transition and multiplicity regime. Panels (a) and (b) show hysteresis loops in reactant coverage and coverage multiplicity respectively as a function of defect concentration. Panels (c), (d), (e) show: 1.2% defect concentration on a 27 × 27 surface, 4% on a 30 × 30 surface, and 7.4% on a 33 × 33 surface respectively for $KP = 0.016$, at $t/\tau_s - 10$.

Figs. 5a and 5b show the influence of concentration of regularly distributed defects on reactant coverage, phase transition, and reactant coverage multiplicity. Panels (c)–(e) are snapshots of the surface for each concentration used in figs. 5a and 5b. Defects with very strong binding energy which can interact through first nearest neighbor attractive forces are nucleation centers which facilitate nucleation. Consequently, the reactant pressure for the transition from a low to a high coverage decreases and the multiplicity regime is reduced, fig. 5b. In addition, the average coverage on the surface is increased and the desorption rate is reduced compared with the perfect surface.

Fig. 6a depicts the isotherms obtained for a 4% constant concentration of defects but different defect distributions shown in figs. 6c–6f. As the number of edge and corner defect atoms increases,

more defects can interact with adsorbed atoms and the number of nucleation centers increases. Therefore, the location of the phase transition is shifted to a lower reactant pressure and the metastability regime becomes more narrow as shown in fig. 6b. The simulations predict that single defect sites distributed either regularly or randomly are more efficient in shifting of the location of the phase transition and in the reduction of the metastability regime.

## 8. Phase transition driven by vacant site requiremen: r reaction

To understand the different bifurcation behavior shown in figs. 3c, f, and i, the adsorption–reaction model with vacant sites in the absence of desorption ($k_{d0} = 0$) is first examined. When two

vacant sites are required for reaction ($m_R = 2$), the model has an analogy with the ZGB model [6] where two vacant sites are required for adsorption of $O_2$ into empty perimeter sites. Our model is also related to the "contact process" where an interacting particle system is used to examine the spread of an infection. In this model, the desorption rate which corresponds to our reaction rate is proportional to the number of empty nearest neighbors (for a discussion see [25] and references therein). Our $m_R = 1$ model is similar to the model studied in one dimension by Dickman and Burschka in which a particle reacts if at least one of the nearest neighbors sites is vacant [25].

Both $m_R = 1$ and $m_R = 2$ models show deviations from MFA in one and two dimensions [33]. For brevity, only the case of two vacant sites for reaction ($m_R = 2$) is presented here in two dimensions. An abrupt phase transition (hereafter called kinetic transition) from a low coverage to a totally covered surface where the reaction rate is zero

(poisoning of reaction) is observed as the reactant pressure increases. This transition which is observed when two vacant sites are needed for reactant decomposition, occurs at much higher pressure than the equilibrium transition studied above (sections 3–7) and is not due to absorbate–absorbate interactions since desorption is not included in most of the simulations of this section. It is of a kinetic character because the overall process is irreversible. In the following, the adsorption–reaction $m_R = 2$ model is examined. Finally, the effect of Langmuir desorption ($w/kT = 0$) and migration on the transition is also discussed.

The MFA predicts that for low pressures ($k_a P/k_R < 0.25$) three solutions exist, fig. 7a. The high-coverage solution corresponds to a poisoned catalytic surface whereas the middle-coverage one is unstable. The only reactive attractor corresponds to the lower coverage. The MC data indicate a discontinuous transition from a low-cover-
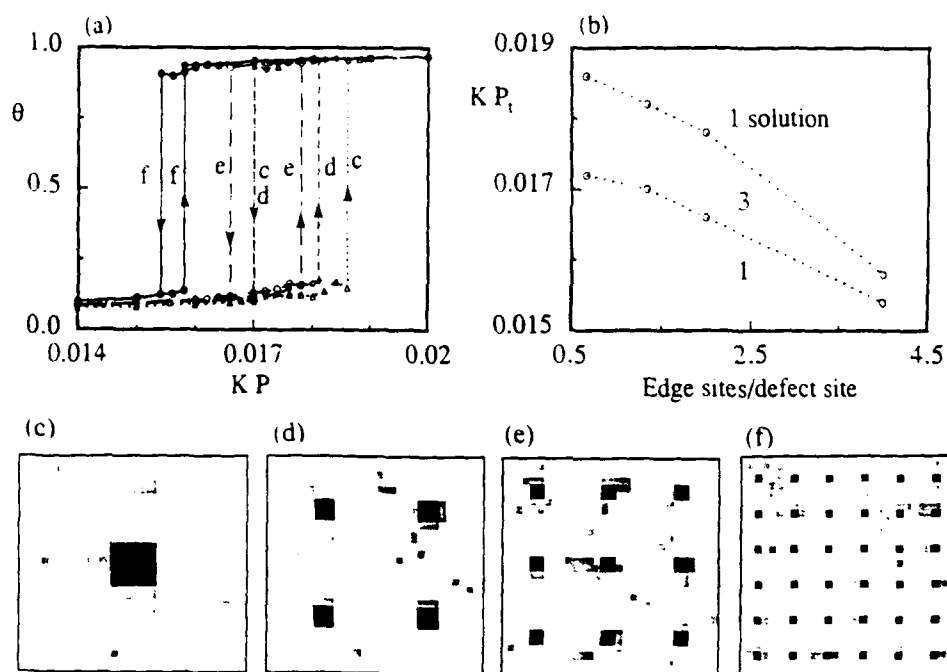


Fig. 6. Influence of distribution of defects on the equilibrium phase transition for 4% defects. In panel (b), edge atoms are counted once and corner atoms twice. The curves (c)–(f) correspond to different distributions of defects as shown in the corresponding panels obtained for $KP = 0.016$, at $t/\tau_s - 15$. The lattice size is $30 \times 30$.

age to a poisoned surface at a pressure much lower than the MF prediction, fig. 7a. At very low reactant pressure, a few atoms are present on the surface and, since they are almost randomly distributed, very good agreement with the MF is found. As the reactant pressure increases, local spatial fluctuations occur which lead to the formation of small clusters. For rectangular clusters, reaction can take place only at their borders. Sites in the interior of the nuclei are inactive. As the reactant pressure increases the cluster size rises and when it reaches a critical value the surface is rapidly poisoned. Starting with totally covered surface and reducing the reactant pressure, no reactive state can be reached without desorption.

The effect of Langmuir desorption ($w/kT = 0$, no diffusion) is shown in fig. 7a for different values of desorption constant, $k_{d0}/k_R$. Desorp-

tion blocks nucleation and unless the desorption probability is much less than the reaction one, no discontinuous transition is observed. Since desorption disintegrates the nuclei, a higher reactant pressure is required for nucleation to occur, i.e. the transition is shifted to the right of the kinetic transition. The creation of holes in the interior of nuclei and the removal of atoms bound at the cluster's periphery result in a lower degree of clustering on the catalyst [33]. The desorption of atoms from the interior of clusters makes them less compact and more molecules can find two vacant sites to deposit the reaction products. Consequently, higher reactivity is achieved, fig. 7b. When desorption is slow, hysteresis loop is formed if we start with a totally covered surface. Hence, desorption is the main process against poisoning of the catalytic surface. Due to desorption, it is
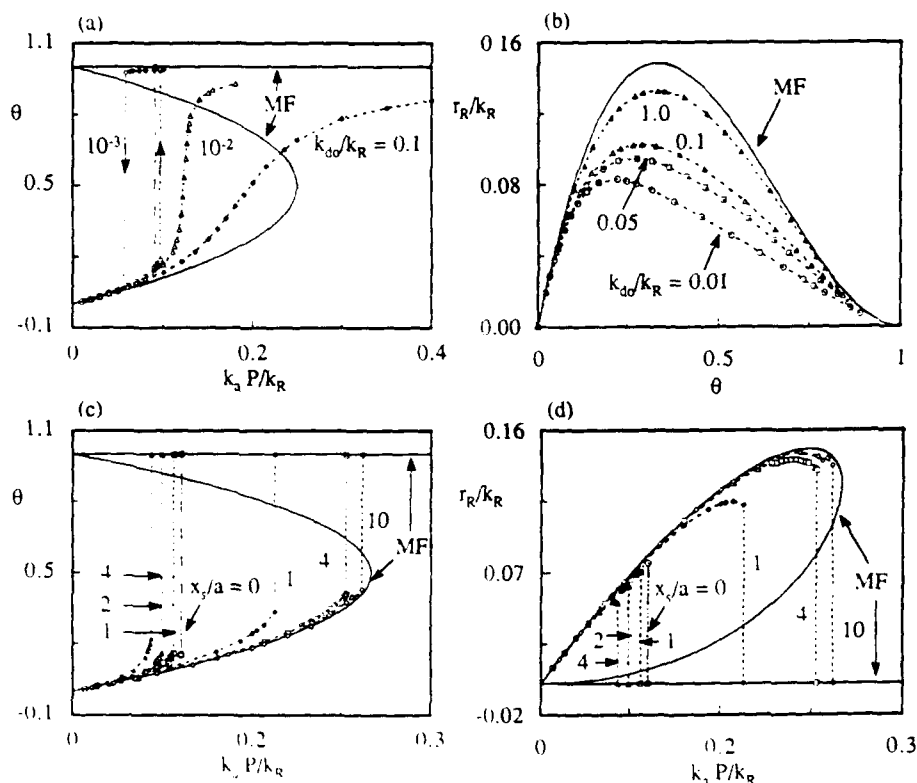


Fig. 7. Phase transition driven by vacant sites requirements for reaction. The kinetic phase transition for $m_R = 2$ in the absence of desorption and diffusion is shown by the dash-dotted line in panels (a) and (c) whereas the MF model is shown by the solid line. Panels (a) and (b) show the effect of Langmuir desorption ($w/kT = 0$) without diffusion whereas panels (c) and (d) show the effect of surface diffusion (in the limit of a very slow desorption) on the reactant isotherm and reaction rate respectively.

possible to maintain a higher coverage on the surface and to increase the maximum reaction rate obtained.

The effect of surface diffusion on the kinetic transition is depicted in figs. 7c and 7d. The curves at the left of the kinetic transition correspond to coverage dependent diffusion coefficient (in the limit of $k_{do} \rightarrow 0$, $w/kT = 2$). When lateral interactions are important, the diffusion sets a driving force for providing atoms to the cluster resulting in bigger clusters on the surface. The steady-state distribution of clusters indicates that in this case fewer single atoms are present on the surface and the size of the largest cluster increases with $x_s/a$ [33]. This increase of coverage and degree of clustering on the catalytic surface leads to more easy poisoning of the catalyst, i.e. shifting of the transition to the left (lower reactant pressure), fig. 7c.

The curves at the right of the kinetic transition correspond to coverage independent diffusion coefficient $(k_{do} = 0$, $w/kT = 0)$, i.e. no interactions between the adatoms. This situation corresponds to a "Fickian kind" of diffusion. In this case single atoms and atoms at the periphery of clusters have equal probability for migration. In the reactant pressure regime where clustering is important and many atoms exist at the periphery of nuclei, on the average more atoms escape from nuclei. The average number of single atoms on the surface increases, and the size of largest cluster decreases [33]. Therefore, the diffusion process randomizes the surface. As the mean displacement $x_s/a$ of the atoms on the surface increases, previously blocked atoms can react. For very large migration rates, the surface has been almost randomized, and the MFA is quite accurate.

Comparison of our $m_R = 2$ model with the ZGB model indicates that the feature of two vacant sites in reaction or adsorption causes a discontinuous transition to a poisoned surface and active steady states $(\theta \neq 1)$ are only possible in two or more dimensions, i.e. in one dimension the chain becomes eventually poisoned [33]. In addition, a Langmuir desorption process can destroy the discontinuous transition and a Fickian diffusion randomizes the surface and shifts the transition to a higher pressure. These observations are

in qualitative agreement with the studies of the role of these processes on the ZGB discontinuous phase transition [5,24].

## 9. Conclusions

Detailed Monte Carlo studies have been used to examine the adsorption–desorption–reaction–diffusion processes for a unimolecular reaction on a catalyst surface using various forms for adsorption, desorption, and reaction rates. Formation of clusters and their subsequent growth has been observed in our two-dimensional simulations along with their profound influence on surface reactions. Phase transitions can be driven either by attractive absorbate–absorbate interactions or by vacant sites required for reactant decomposition. In both cases abrupt first-order transitions have been found for appropriate values of the parameters. The existence of discontinuous transitions is usually associated with hysteresis loops which indicate multiplicity in coverage and desorption–reaction rates.

The MF theory is qualitatively correct in two dimensions in predicting the existence of multiple solutions and cusp points. However, large deviations in coverage and desorption–reaction rates can be found between MF theory and MC simulations. In general, the formation of clusters caused by any reason cannot be treated correctly by the MFA because of its uniform coverage assumption. Other investigations of bimolecular systems of reactants A and B without any attractive interactions or vacant sites requirements indicate that deviations between the MF model and MC data would be expected if the desorption rate constants of the reactants are small so that the randomization of atoms on the surface is slow [33]. Thus, the nonlinearity in the reaction term, $r_R = k_R \theta_A \theta_B$, can result in inaccuracy of the MF theory [33]. Therefore, our calculations and the recent MC studies of vacant sites requirements in adsorption of one of the two reactants in a bimolecular system [6] suggest that whenever a nonlinear term appears in the ordinary differential equations describing the dynamics of the system, the MF theory can be only an approximation. The error in

the approximation depends on the values of the parameters, the importance of migration, and surface defects.

MC simulations reveal that, when nucleation occurs, the existence of a Langmuir process (reaction in the case of equilibrium transition and desorption in the case of kinetic transition) destroys nucleation and prevents the filling of the surface which causes poisoning of the surface reaction when vacant sites for reaction are required. A study of the influence of migration on nucleation and phase transitions indicates that, if the diffusion coefficient is concentration independent, migration randomizes the distribution of atoms and makes the MFA more accurate. However, in the presence of attractive interactions, migration can facilitate cluster formation and drive the system faster to the stable steady state, making the MFA worse.

The most severe limitations of the MF theory concern its incapability to predict the existence of metastable states and the fluctuations of the system occurring in a small surface region. The dynamic behavior of a reactive irreversible system around a cusp point is very important, because the very large fluctuations can be confused with the oscillations seen in experiments. The analysis of dynamics at cusp points is important to distinguish from the periodic patterns observed in real experiments. The question of when these fluctuations are related to global periodic oscillations is investigated elsewhere [7].

In addition, no information can be obtained from the MF theory about the influence of migration on the transition from the metastable state to the stable state. The influence of diffusion on kinetic transitions and on Hopf bifurcation, as demonstrated elsewhere [7], is totally missing from the MF theory. Furthermore, inhomogeneities in binding energy with the substrate and the existence of point and line defects which are of great practical importance in real experiments cannot be handled at all by the MFA. Microscopic models, such as Monte Carlo and molecular dynamics simulations, in combination with the new surface techniques could provide insight in the dynamics of heterogeneous processes.

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