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Chemical diffusivity and wave propagation in surface reactions

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Chemical diffusivity and wave propagation in surface reactions

by

Michael Joseph Tammaro

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in partial fulfillment of the requirements for the degree of
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Iowa State University
Ames, Iowa
1997

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CHAPTER 1. GENERAL INTRODUCTION

Introduction

The subject matter of this thesis is the theoretical study of chemical reactions on metal surfaces. Experimentally, the most intensively studied reactions are CO-oxidation and NO-reduction [1-7]. Theoretically, the approach is to formulate and analyze simple models that capture the essential features of the real systems. One of the basic goals of analysis is to determine the steady states of the system. In a CO-oxidation model, for example, there may be a range of model parameters where surface is completely covered with CO and another range where there is a low CO concentration and high reactivity. Such “phases” can be mapped as a function of model parameters to construct the phase diagram. Some models are known to produce robust phase diagrams and, besides the obvious importance of connection to experiment, the study of these models can be considered equally important as an abstract problem in pure statistical physics.

These systems are far-from-equilibrium and therefore outside the realm of classical equilibrium statistical mechanics. Furthermore, since the transition rates do not satisfy detailed-balance, there is no fluctuation-dissipation theorem, and linear response theory does not generally apply. Despite considerable interest in far-from-equilibrium systems [8-16], the theories developed thus far are much less adequate than their equilibrium counterparts, and therein lies the challenge for researchers in this field.
The focus of this work has been on two generally distinct features of these systems. One is the phase diagram, critical points, phase transitions and fluctuations. The other is the detailed description of adspecies diffusion, via determination of the correct chemical or collective diffusion coefficient, whose importance lies in studying the propagation, across the surface, of an interface between distinct phases. In this work, a number of methods have been employed to study these phenomena, but the majority of the results have relied on lattice-gas modeling, the analysis of mean-field rate equations, and reaction-diffusion equation analysis. Below, two of the most important models are introduced as well as a brief description of the methods of analysis.

The AB$_2$ Model For CO-Oxidation

The AB$_2$, or “monomer-dimer”, model mimics CO-oxidation on single crystal surfaces. The surface is assumed to be a square lattice of adsorption sites. This choice is best not only in terms of computational and analytical ease, it is also corresponds to the experimentally important Pd(100) and unreconstructed Pt(100) planes. Since CO does not dissociate when it adsorbs onto the surface, it will be represented by a generic “monomer” species, A. When oxygen, O$_2$, adsorbs it dissociates and becomes two single oxygen atoms. Oxygen will be represented by a generic “dimer” species, B$_2$, and empty surface sites will be represented by E. The steps of the model are as follows:

$$A(g) + E \rightarrow A(\text{ad})$$

$$B_2(g) + 2E \rightarrow 2B(\text{ad})$$
\[ A^{(ad)} + B^{(ad)} \rightarrow AB^{(g)} + 2E \]

Here \((g)\) represents gas phase, and \((ad)\) represents adsorbed phase. In the first step \(A^{(g)}\) impinges on the surface. If it finds an empty site on the surface, it will occupy it, becoming \(A^{(ad)}\). In the second step \(B_2^{(g)}\) impinges on the surface, dissociating if it finds two empty sites to become two \(B^{(ad)}\) atoms. In the third step adjacent \(A^{(ad)}\) and \(B^{(ad)}\) react to form \(AB^{(g)}\) leaving two empty sites. This model is the generic \(AB_2\) model and will be studied extensively in this work. In order to study the model, adsorption and reaction rates must be specified as well as the microscopic rules for these processes. In addition to the above steps cases will be considered where \(A^{(ad)}\) spontaneously desorbs, \(A^{(ad)}\) is allowed to diffuse by hopping to adjacent empty sites, and both \(A^{(ad)}\) and \(B^{(ad)}\) are allowed to diffuse.

The impingement rate (sometimes referred to as "pressure") for \(A^{(g)}\) is denoted by \(y_A\), and for \(B_2^{(g)}\) it is \(y_B = 1 - y_A\). The reaction rate for \(AB^{(g)}\) formation is commonly chosen to be \(k = 1\) or \(\infty\). The latter choice, with instantaneous reaction, is the ZGB model \([8]\) which is studied in Chapter 2. Regardless of the choice of reaction rate, the qualitative features of the model do not change. The conventional phase diagram for the \(AB_2\) model is a plot of the coverage of \(A\), \(\theta_A\), versus \(y_A\). (\(\theta_J\) is called the coverage of species \(J\), and is simply the fraction of surface sites occupied by \(J\).) Fig.1 is a sample of a steady state phase diagram for the \(AB_2\) model where there is no diffusion or spontaneous desorption of \(A^{(ad)}\) or \(B^{(ad)}\). For \(y_A < y_1\) the steady state is a \(B\)-poisoned state, in which the surface is completely covered with \(B^{(ad)}\). For \(y_A > y_2\) the steady state is an \(A\)-poisoned state, in which the surface is completely covered with \(A^{(ad)}\). For \(y_1 < y_A < y_2\) the system is in a reactive steady state where adsorption and reaction events are taking place, but there are well defined average coverages \(\theta_A\) and \(\theta_B\). (If
Fig. 1 Steady state phase diagram for the $\text{AB}_2$ surface reaction model, from Monte Carlo simulations.
A(ad) is allowed to desorb spontaneously, the state for $y_A > y_2$ becomes a high-$\theta_A$ reactive steady state.) The pressure $y_1$ is the location of the continuous transition from the reactive steady state to the B-poisoned state, and $y_2$ is the location of the discontinuous transition from the reactive steady state to the A-poisoned state. Note that for the case where no spontaneous desorption of A(ad) or B(ad) is allowed, the poisoned states are absorbing states, so the transitions to these states are irreversible.

The NO+CO Reaction Model

This model describes NO-reduction by CO on a pre-covered Pt(100) surface. Again we consider a square lattice of adsorption sites. The steps for this reaction are as follows:

\[
\begin{align*}
\text{NO(ad)} + \text{E} & \rightarrow \text{N(ad)} + \text{O(ad)} \\
\text{CO(ad)} + \text{O(ad)} & \rightarrow \text{CO}_2(g) + 2\text{E} \\
\text{N(ad)} + \text{N(ad)} & \rightarrow \text{N}_2(g) + 2\text{E}
\end{align*}
\]

In this model, there is no adsorption or desorption of reactant species. The first step is the spontaneous dissociation of an NO(ad) molecule, requiring an adjacent empty site. The second step is the reaction between CO(ad) and O(ad), leaving two empty sites, and the third step is the reaction between two N(ad) atoms, also leaving two empty sites. If the surface is completely covered with NO(ad) and CO(ad) such that $\theta_{\text{NO}} + \theta_{\text{CO}} = 1$, then since NO(ad) and CO(ad) do not react, and there are no empty sites for NO(ad) to dissociate, this is a steady state. However, if one introduces a small number of empty sites, NO(ad) will dissociate, and suddenly the reaction steps become possible, leaving still more empty sites. This
autocatalytic removal of the NO-CO adlayer produces a traveling reaction-diffusion front.

One focus of this thesis has been to accurately determine the velocity of these traveling fronts by deriving the correct chemical diffusion coefficients for mixed adlayers.

Mean-Field Rate Equation Analysis

The mean-field rate equations are used to describe the reaction kinetics of a spatially uniform system. Here the distribution of molecules on the surface is assumed to be random. The probability that a site is occupied with a species \( J \) is simply \( \theta_J \), and differential equations for the time evolution of these coverages can be written. For the \( \text{AB}_2 \) model, with no spontaneous desorption of \( \text{A(ad)} \) or \( \text{B(ad)} \), one has

\[
\frac{d\theta_A}{dt} = y_A \theta_E - 4k\theta_A \theta_B
\]

\[
\frac{d\theta_B}{dt} = 2y_B \theta_E^2 - 4k\theta_A \theta_B
\]

The terms in these equations can be readily understood. For example, the second term in each equation represents the reaction between adjacent \( \text{A(ad)} \) and \( \text{B(ad)} \), at rate \( k \), where \( \theta_A \theta_B \) is the probability of a given pair being an \( \text{AB} \) pair. (This probability can be written as the product \( \theta_A \theta_B \) only in the mean-field limit, where we assume there are no spatial correlations.) The same term appears in both equations because \( \text{A(ad)} \) and \( \text{B(ad)} \) leave the surface only in pairs. The first terms are the adsorption terms and are also easily understood.

To find the steady state phase diagram, one must set the LHS equal to zero, and solve the resulting algebraic equations. The resulting phase diagram is shown in Fig.2. Instead of
Fig. 2 Steady state phase diagram for the AB₂ model using mean-field rate equations. For \( y_A < 0.5 \), the reactive steady state and the A-poisoned state are both stable.
the discontinuous transition, there is a spinodal point at $y_S=0.5$ separating a region of bistability for $y_A<y_S$ with a single steady state for $y_A>y_S$. Also, the continuous transition is not present, extending the reactive steady-state to $y_A=0$. The utility of this type of analysis is that these equations can describe, fairly well, the time evolution and steady states of a spatially uniform system away from critical points, where spatial correlations are small.

For any non-equilibrium model, one can write down exact master equations, which take the form of an infinitely coupled hierarchy, for the probabilities of various configurations of sites. Approximate solution is possible by neglecting all but a limited set of short range correlations in so called “dynamic-cluster” approximations. The simplest is the “site” approximation (equivalent to the mean-field approximation), where all spatial correlations are ignored.

Mean-Field Reaction-Diffusion Equation Analysis

Analysis of spatial inhomogeneities in these models, using reaction-diffusion equations, is a major part of this work. The mean-field rate equations can be sufficient to describe the temporal behavior and steady states of a spatially uniform system. Recently, however, there has been increasing interest in describing chemical wave propagation in these systems [17]. Wave propagation arises when the system is in a region of the phase diagram where there is bistability. Two phases coexist and, depending on the relative stability of the two phases, one will displace the other and form what is called a chemical wave. Reaction-diffusion equations are simply mean-field rate equations with diffusion terms “added on”.

For the AB$_2$ model, if we assume a constant chemical diffusion coefficient, $D_A$, for A(ad), and that B(ad) is immobile, the equations become

$$\frac{\partial \theta_A}{\partial t} = y_a \theta_A - 4k \theta_A \theta_B + D_A \frac{\partial^2 \theta_A}{\partial \theta_A^2}$$

$$\frac{\partial \theta_B}{\partial t} = 2y_B \theta_B^2 - 4k \theta_A \theta_B$$

The assumption that $D_A$ is a constant, and does not depend upon either $\theta_A$ or $\theta_B$, will be shown to be a crude approximation. Determining the correct form of the chemical diffusion coefficient is one of the major aspects of this thesis.

These equations can be analyzed by discretizing space, and keeping time continuous. The coupled partial differential equations become a system of coupled ordinary differential equations and can be integrated using a variety of standard numerical routines. This technique is called the method of lines. [18] A typical wave profile using this method is shown in Fig.3. Typically, a reaction-diffusion equation analysis of this kind focuses on measuring the shape of the profile, and the velocity of the chemical wave, as a function of $y_A$.

Monte-Carlo Simulations

Monte Carlo modeling is an indispensable technique for the statistical physicist. Monte Carlo simulations can essentially reproduce the exact behavior of a model. This is extremely important, not only in terms of obtaining accurate results, but also in terms of assessment of approximation methods. This point is further strengthened when one realizes that there are very few exactly solvable problems in statistical physics. (The most famous
Fig. 3 Chemical wave profile for the AB₂ model using reaction-diffusion equation analysis.

This figure depicts the reactive steady state phase displacing the A-poisoned phase at y_A=0.4.
exactly solved problem is Onsager's exact solution for the 2-D Ising Model [19].) However accurate, it is important to understand the limitations of these simulations. The finite memory of the computer places limitations on the size of the systems studied, and finite size effects must be understood. The quality of the random number generator can also be an important factor if it produces unwanted correlations in the model. These and other factors must be understood and tested before any simulation data can be taken seriously. Because the models studied here are non-equilibrium, without detailed-balance, the traditional Metropolis Monte Carlo algorithm does not apply. Rather, these simulations are called Monte Carlo because of the central role the random number generator plays in the simulations. The Monte Carlo technique properly accounts for all correlations and fluctuations in the model. For studying critical behavior, where correlations and fluctuations dominate, Monte Carlo simulations are indispensable.

As an example, consider the AB$_2$ model with no diffusion. Start with a 2-D matrix that represents the square lattice. The total rate of events happening is $\Gamma = y_A + y_B + k$ with $y_A + y_B = 1$ and $k = 1$. A typical trial proceeds as follows. Attempt an adsorption or reaction event with equal probability. (In general, the reaction and adsorption probabilities are not equal but, because of the specific choice of rates, they are in this case.) If reaction is chosen, pick a random nearest neighbor pair of sites. If occupied by an AB pair, remove them, leaving a pair of empty sites. If adsorption is chosen, pick A with probability $y_A$, and B$_2$ with probability $y_B$. If A is chosen, pick a random site, and if it is empty, it becomes A(ad). If B$_2$ is chosen, pick a random pair of sites, and if both are empty, occupy them with B(ad).
Dissertation Organization

This thesis is a compilation of work that has either been published, submitted for publication, or is in preparation for submission. Each paper is a separate chapter. Chapter 2 is a paper, published in Physical Review E, which studies the influence of the dimer adsorption mechanism on the phase transitions in the $\text{AB}_2$ model. Chapter 3 studies chemical wave propagation and the critical point in a "hybrid" $\text{AB}_2$ model. The hybrid model combines a mean-field treatment of the mobile A species and a lattice-gas treatment of the immobile B. This paper was published in the Journal of Chemical Physics. Chapter 4 is a paper published in the Journal of Chemical Physics, which studies the "percolative" nature of the CO diffusion in a CO-oxidation model using reaction-diffusion equations. Chapter 5 is a paper that studies chemical diffusion in mixed adlayers. Emphasis is on characterization of the intrinsic non-linearities that are due to the influence of the coadsorbed species. This paper has been submitted to Physical Review Letters. Chapter 6 studies chemical wave propagation in the $\text{AB}_2$ model and emphasizes the need for the non-linear description of diffusion from chapter 5. This paper has been submitted to the Journal of Chemical Physics. Chapter 7 studies, in detail, adlayer removal in the NO-CO reaction model. The theory of chapter 5 is applied to chemical wave propagation in this model. In chapter 8 are some general conclusions.

References


CHAPTER 2. THE MONOMER-DIMER SURFACE REACTION MODEL: INFLUENCE OF THE DIMER ADSORPTION MECHANISM

A paper published in Physical Review E.

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ABSTRACT

We consider the monomer-dimer surface reaction without surface diffusion for various dimer adsorption mechanisms, as now described. After dimer impinges "end-on" at an empty site, its bottom atom remains there while its top atom searches \(N \geq 1\) sites, either in a local neighborhood (\(N\)-local models), or randomly located on the surface (\(N\)-random models), to find a second empty site. If one is found, then the dimer can then adsorb dissociatively. The \(N\)-local models have a reactive window of finite width in the relative impingement rates bordered by poisoning transitions, whereas the \(N\)-random models exhibit true bistability. As \(N\) increases, the reactivity is either strictly or effectively confined to relative impingement rates close to the stoichiometric ratio. We precisely analyze the limiting behavior as \(N \to \infty\).
1. INTRODUCTION

It is instructive here to consider first a rather general class of surface reaction models involving molecules $A_m$ of $m$ A-atoms, and $B_n$ of $n$ B-atoms, and which include the following steps

$$A_m(g) + mE \rightarrow mA(ads)$$

$$B_n(g) + nE \rightarrow nB(ads)$$

$$A(ads) + B(ads) \rightarrow AB(g) + 2E$$

Here (g) represents a molecule in the gas phase, (ads) represents an adspecies, and E represents an empty adsorption site. We assume that $A_m(g)$ impinges on the surface with rate $P_A$, and $B_n(g)$ with rate $P_B$, and that these species dissociatively adsorb if they find appropriate ensembles of empty sites. We normalize $P_A + P_B$ to unity. Adjacent adsorbed species of different types react to form $AB(g)$ at rate $k$, which could be infinitesimal, finite, or infinite. In general, there may be adspecies mobility. For a steady state to exist, since the removal rates for species A and B are necessarily always equal, it follows that the adsorption rates for both species must also be equal. It is important to note here the following distinction. The impingement rate is the rate at which adsorption events are attempted (successful or not), while the adsorption rate is the rate of successful adsorption attempts multiplied by the number of atoms in the adsorbing molecule.
If \( m=n \), and both \( A_m(g) \) and \( B_m(g) \) adsorb randomly on identically shaped configurations of empty sites, then clearly the ratio of the adsorption rates for species A and B is exactly equal to the ratio of the impingement rates (independent of the statistics of the adlayer). Therefore a reactive steady state is only possible if \( P_A=P_B \). If there is an imbalance in impingement rates, then the species with the higher impingement rate will poison the surface. This behavior is well known for the monomer-monomer or A+B reaction model (\( m=n=1 \)). Here it is also known that no true steady state exists even when \( P_A=P_B \), but that the system slowly poisons as domains of A(ad) and B(ad) grow in size. Behavior is analogous to that of the two-dimensional (2D) Voter model. Presumably poisoning also occurs when \( P_A=P_B \) for \( m=n>1 \), except that the poisoned state will be a non-trivial jammed state incorporating empty sites, but no adsorption ensembles of \( m=n \) empty sites\(^2\). Also the kinetics of poisoning may differ from when \( m=n=1 \), but will no doubt still be slow. In contrast, if one introduces symmetry-breaking cooperativity into the adsorption process, then in general the ratio of the adsorption rates will depend on the adlayer statistics. A reactive steady state can potentially be achieved for a range of \( P_A \neq P_B \) by adjustment of the adlayer statistics. The width or extent of this reactive regime clearly vanishes as one "switches off" the cooperativity. A key question is then whether this width vanishes continuously, or rather at a non-trivial "tri-critical point", for some non-zero degree of cooperativity. Zhuo et al\(^5\) studied of a cooperative monomer-monomer reaction, where the adsorption rate of \( A(g) \) at empty sites with \( n \) neighboring A(ads) is now given by \( r^\theta P_A \), but B(g) adsorption remains random at rate \( P_B \). They suggested the existence of a tri-critical point at some \( r=r_c<1 \), below the \( r=1 \) non-cooperative limit.\(^5\)
For m≠n, invariably the ratio of adsorption rates for species A and B will depend on the adlayer statistics. Thus a reactive steady state can potentially be achieved for a range of P_A, again by suitable adjustment of the adlayer statistics. This is well known for the most intensively studied case of the monomer-dimer or A+B_2 reaction model where m=1 and n=2, and where B_2(g) adsorbs on adjacent pairs of empty sites. Within the context of modifying the extent of reactivity, we comment on behavior in the reaction-limited regime as k→0.

When k=0+, the surface is completely covered. After each reactive removal of an adjacent AB-pair, the created empty pair is immediately filled, either by a single B_2(g) species, or sequentially by two A(g) species. Clearly here the adsorption rates are simply in proportion to the impingement rates, and are equal when P_A:P_B=1:4. In this case, the model exhibits slow poisoning due to coarsening of domains of A(ad) and B(ad), analogous to the 2D Voter model, and the monomer-monomer model when P_A=P_B (see Ref.4). For the case of immobile adspecies, the reactive window narrows with decreasing k, and was first proposed to vanish at a non-zero tri-critical value of k. However more recent studies suggest that its width vanishes continuously as k→0.

Here we consider the effect on the monomer-dimer or A+B_2 reaction model of modifying the standard dimer adsorption mechanism. We consider only immobile adspecies and instantaneous reaction of adjacent AB-pairs (k=∞). In the standard model, one randomly picks an empty site, and then randomly selects one neighbor, adsorbing if it is also empty. In the modified models, we search for a second empty site amongst a local neighborhood of N≥1 sites (N-local adsorption), or from amongst N≥1 other randomly chosen sites on the
lattice (N-random adsorption). In either case, as $N \to \infty$, a second empty site will certainly be found, so the adsorption rates for $A(g):B_2(g)$ are in the proportion $P_A:2P_B$. Thus steady state reaction cannot be sustained if $P_A \neq 2P_B$, as $N \to \infty$. Here we provide a detailed analysis of the associated continuous decrease in the width of the reactive window for N-local models, and of the continuous shrinkage of the regime of significant reactivity for N-random models, with increasing $N$.

2. MODEL DESCRIPTIONS

The monomer-dimer surface reaction model

\[
A(g) + E \to A(ads) \\
B_2(g) + 2E \to 2B(ads) \\
A(ads) + B(ads) \to AB(g) + 2E
\]

mimics CO-oxidation on single crystal substrates, with $A$ corresponding to CO, and $B_2$ to $O_2$. Here $A(g)$ requires a single empty site to adsorb, and $B_2(g)$ requires an empty pair, which will not necessarily be adjacent in our prescriptions below. We assume that only adjacent AB-pairs react, and that this occurs instantaneously. Below we also set $P_A=y$ and $P_B=1-y$. We shall consider only a square lattice of adsorption sites.

2.1 N-Local Adsorption

The dimer adsorption mechanism in these models can be described as follows. An empty site is chosen at random, and then a local neighborhood of $N$ sites is sampled in a
fashion prescribed below, adsorption of $\text{B}_2(\text{g})$ occurring if at least one empty site is found in this neighborhood. For $N=1$, one nearest neighbor is chosen at random, and our model corresponds to the standard Ziff-Gulari-Barshad (ZGB) monomer-dimer reaction model\textsuperscript{6}.

Next we discuss the case $N=4$. Here all four (hence $N=4$) nearest neighbors of the first empty site are checked for vacancies. If any are found, then one is chosen randomly to accommodate the second $\text{B(ad)}$. The $N=1$ model is equivalent to randomly selecting adjacent pairs of empty sites, which might be thought of as dimer adsorption through a horizontal transition state. In contrast the $N=4$ model more reflects adsorption through a vertical transition state, where the lower end of the dimer attaches to an empty site (at least transiently), while the upper end searches for an empty neighbor. See Ref.\textsuperscript{11}.

Dimer adsorption in the $N=8$ model proceeds as for $N=4$, but if a second empty adsorption site is not found in the first nearest neighbors, then the second nearest neighbors are checked for vacancy. If any are found, then one is chosen randomly from them. For the $N=12$ model, if no vacancies are found amongst the first and second nearest neighbors, then the third nearest neighbors are checked and one selected at random (if any are found). The next case in this sequence where one searches “shell by shell” for a second adsorption site is $N=20$ because there are 8 fourth nearest neighbors on a square lattice (Fig.1a). Models for intermediate $N$-values could also be considered, as well as various other prescriptions of neighborhoods and searching procedures.

For the $N=1$ ZGB model, simulations have shown\textsuperscript{12,13} that a reactive steady state exists only for $y_1=0.3906 < y < y_2=0.5256$. There is a continuous transition to a $\text{B}$-poisoned state as $y$ decreases below $y_1$, and a discontinuous transition to an $\text{A}$-poisoned state as $y$ decreases
Fig. 1 (a) "Adsorption neighborhoods" in the N-local models, for various N. If the center site (indicated by 0) is empty, then the bottom B-atom in the dimer lands there, while the top B-atom searches the other sites (indicated by O) for a second vacancy. (b) An alternative geometry for the N=8 model.
below \( y_1 \), and a discontinuous transition to an A-poisoned state as \( y \) increases above \( y_2 \). These poisoned states, where every lattice site is occupied with A or B are "adsorbing" since there is no spontaneous desorption of adatoms. One might expect this general picture to apply for \( N>1 \), but that the location of these transitions shift, and that the width, \( \Omega = y_2 - y_1 \), of the reactive window decreases, with increasing \( N \). We provide a detailed analysis of these trends in Sec.3, but first present some analytic results.

Because \( A(g) \) only needs a single empty site to adsorb, the (total) adsorption rate for A is \( Y_A(T) = yE \) where \( E \) denotes the concentration of empty sites on the surface. The (total) adsorption rate for B is \( Y_B(T) = 2(1-y)EQ \), where \( Q \) is the conditional probability that if a single empty site is found, then another empty site will be found in the prescribed neighborhood of \( N \) sites. Note that \( Q \) depends only on the size, \( N \), and on geometry of the neighborhood, but not on the order in which the sites are sampled. The presumably weaker dependence on this order will appear in the hierarchic rate equations for the probabilities for multisite configurations. Since the reaction mechanism guarantees that the removal rates of A and B are equal, in a steady state, one must have \( Y_A(T) = Y_B(T) \). This implies that either \( E = 0 \) (poisoned state), or \( Q = y(1-y)^{1/2} \leq 1 \). Since the second condition cannot be satisfied for \( y > 2/3 \), it follows that only poisoned states exist in this region. Furthermore since trivially \( Y_A(T) > Y_B(T) \) for \( y > 2/3 \), the system will always evolve to an A-poisoned state (unless initially B-poisoned). Consequently one has \( y_1 \leq y_2 \leq 2/3 \).

Next consider evolution of the model through non-poisoned states, for fixed \( y < 2/3 \). Since \( Q \to 1 \), as \( N \to \infty \), it follows that \( Y_B(T) > Y_A(T) \), so the system must evolve to a B-
poisoned state. This implies that either $y_1 \to 2/3$, as $N \to \infty$, or perhaps that $y_1$ remains below 2/3, as $N \to \infty$, but that the B-coverage approaches unity (and the reaction rate vanishes) in the reactive steady state. In either case, one necessarily has $y_2 \to 2/3$, as $N \to \infty$, and we shall see that the same is true for $y_1$ (for this model).

2.2 N-Random Adsorption

Here the dimer adsorption mechanism is such that after a first empty site is selected randomly, one checks up to $N$ other randomly located sites on the lattice, and adsorbs the dimer if and when one of these is found to be empty. In this model, one has $Y_A(T) = yE$ and $Y_B(T) = 2(1-y)E[1-(1-E)^N]$. The latter quantity can be obtained exactly in contrast to the N-local adsorption model. Thus in a steady state, where these rates are equal, one has exactly

$$\frac{y}{2(1-y)} = 1 - (1-E)^N$$

(or $E=0$ for a poisoned state). This immediately shows that $E \to 0$ continuously, as $y \to 0$, in the reactive steady state, so non-trivial continuous B-poisoning transitions cannot occur in this model, and consequently $y_1=0$ for all $N$. One might expect these models to support a discontinuous A-poisoning transition for $y<2/3$, as did the N-local adsorption models. However below we shall see that instead they display true bistability for all $N$, i.e., for $0<y<y_b$ (a spinodal), a stable reactive steady state and stable A-poisoned state coexist. The stable A-poisoned state at $y=0$ is joined to the stable reactive state at $y=y_b$ by an unstable steady state branch, to form a van der Waals type loop. For $y>y_b$, only the A-poisoned state is stable. In
the \( N \to \infty \) limit, we again have \( Y_B(T) > Y_A(T) \) for \( y < 2/3 \), so it is clear that \( y_c \to 2/3 \), and that the B-coverage of the reactive steady state for any \( y < 2/3 \) must approach unity, as \( N \to \infty \).

3. SIMULATION RESULTS FOR N-LOCAL ADSORPTION MODELS

Our goal is a precise analysis of the vanishing width of the reactive window as \( N \to \infty \). This is complicated both by the presence of a "long-lived" metastable reactive state just above the discontinuous transition\(^{2,8,13}\), and by the presence of large fluctuations at the continuous transition\(^{12}\) which could influence behavior across the entire (narrow) reactive window.

3.1 The Discontinuous Transition: Constant Coverage Analysis

We circumvent metastability problems by utilizing a constant-coverage kinetic ensemble\(^{13}\) to locate the transition, \( y_2 \). (The danger is that a conventional simulation will tend to overestimate \( y_2 \) due to strong metastability\(^8\).) In conventional simulations, a fixed value of \( y \) is chosen and \([A]\) is monitored. In the constant-coverage ensemble, a fixed value of \([A]\) is chosen, say \([A]_0\). Whenever \([A] < [A]_0\), an attempt at \( A \) adsorption is made, and whenever \([A] > [A]_0\), an attempt at \( B_2 \) adsorption is made. One obtains \( y \) as the asymptotic fraction of \( A \) adsorption attempts to the total number of attempts. Since the value of \([A]\) jumps from some typically small value (<0.1) to unity at the discontinuous transition, by choosing \([A]_0 = 0.5\), this guarantees that the associated \( y \)-value will correspond to \( y_2 \). The results are shown in Table 1. These runs were performed on a 300x300 lattice for 100000 timesteps. Note that fluctuations in \( y \) are reduced for large \( N \). Here dimer adsorption is effectively contingent on
Table 1. N-local models. Discontinuous A-poisoning transition location, $y_2$, determined using a constant-coverage analysis.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$y_2$</th>
<th>$2/3-y_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.52560</td>
<td>0.14107</td>
</tr>
<tr>
<td>4</td>
<td>0.65520</td>
<td>0.01146</td>
</tr>
<tr>
<td>8</td>
<td>0.66439</td>
<td>0.00227</td>
</tr>
<tr>
<td>12</td>
<td>0.66574</td>
<td>0.00092</td>
</tr>
<tr>
<td>20</td>
<td>0.66633</td>
<td>0.00033</td>
</tr>
<tr>
<td>24</td>
<td>0.66644</td>
<td>0.00022</td>
</tr>
<tr>
<td>28</td>
<td>0.66652</td>
<td>0.00015</td>
</tr>
<tr>
<td>36</td>
<td>0.666575</td>
<td>0.000092</td>
</tr>
<tr>
<td>44</td>
<td>0.6666078</td>
<td>0.0000589</td>
</tr>
</tbody>
</table>
finding just one empty site, like monomer adsorption. Thus the situation is similar to the monomer-monomer model, where we also find very small fluctuations (about $y=1/2$) in a constant-coverage simulation.

One may ask if there is a sizable dependence of the location of the transitions upon the particular geometry of the prescribed neighborhood of $N$ sites. We determined the location of the discontinuous transition in the model for $N=8$ with a different geometry (nearest neighbors and third nearest neighbors, Fig.1b), and found only a small variation (about 0.6%) from the location for the original $N=8$ geometry shown in Fig.1a.

3.2 The Continuous Transition: Epidemic Analysis

We determine the location of the continuous transition, $y_1$, by means of an epidemic analysis\textsuperscript{12}, wherein one monitors the evolution of an initially empty patch (in this case a single site) on an otherwise B-poisoned surface. We determine the "survival probability" $P(t)$, that the patch has not become B-poisoned at time, $t$, for various values of $y$. $P(t)$ should saturate at a non-zero asymptotic value for $y>y_1$, where there is a finite probability of indefinite growth. However, $P(t)$ should decrease exponentially for $y<y_1$, where ultimate extinction is certain. However at $y_1$, the survival probability is expected to scale like\textsuperscript{12} $P(t)\sim t^{-\delta}$. For the ZGB model, analysis has shown\textsuperscript{12} that this transition is in the universality class of Reggeon Field Theory (RFT), where $\delta=0.452\pm0.008$. This is also expected to be the case for all $N>1$. Following Jensen et al\textsuperscript{12}, we examine the local slope

$$\delta(t) = \frac{\log[P(t)/P(t/5)]}{\log(5)}.$$
As $t \to \infty$, the local slope should curve upwards (approaching zero) for $y > y_1$, and it should curve downwards (approaching $-\infty$) for $y < y_1$. At $y = y_1$, the local slope should converge to the RFT value of $\delta$. Behavior of $\delta(t)$ for $N=1, 4, 8, 12, \text{ and } 20$ is shown in Fig. 2, and the results are summarized in Table 2. Note that if one writes $\delta(t) = 0.452 + a/t$, as $t \to \infty$, then ‘$a$’

Table 2. N-local models. Continuous B-poisoning transition location, $y_1$, determined using an epidemic-analysis, and the associated width of the reactive window obtained also using $y_2$-values from Table 1.

<table>
<thead>
<tr>
<th>N</th>
<th>$y_1$</th>
<th>$y_2 - y_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.391</td>
<td>0.135</td>
</tr>
<tr>
<td>4</td>
<td>0.633</td>
<td>0.022</td>
</tr>
<tr>
<td>8</td>
<td>0.654</td>
<td>0.011</td>
</tr>
<tr>
<td>12</td>
<td>0.6610</td>
<td>0.0048</td>
</tr>
<tr>
<td>20</td>
<td>0.66475</td>
<td>0.0016</td>
</tr>
</tbody>
</table>

changes from positive sign when $N=1$, to negative sign for all $N>1$. Another quantity of interest is the average number of empty sites in the patch as a function of time, $N(t)$. It is possible to perform an analysis identical to that for the survival probability. At the transition, this quantity is expected to scale like $N(t) \sim t^{-\eta}$ with RFT $\eta = 0.224 \pm 0.010$. Behavior for $N=12$ of the corresponding local slope, $\eta(t)$, defined analogous to $\delta(t)$, is shown in Fig. 3.
Fig. 2 Epidemic analysis of the survival probability, $P(t)$, for the N-local models. Plotted is the local slope, $\delta(t)$, vs. $1/t$. Here the transition, $y = y_c$, is determined from the requirement that $\delta(t) \to 0.452$, as $t \to \infty$. 
Fig. 3 Epidemic analysis of the average number of empty sites, $N(t)$, for the $N$-local model with $N=12$. Plotted is the local slope, $\eta(t)$, vs. $1/t$. Here the transition is determined from the requirement that $\eta(t) \to 0.224$ as $t \to \infty$. 
and is consistent with RFT. The survival probabilities were calculated using data averaged
over 50000 to 150000 trials.

3.3 Scaling Behavior

We now propose two scaling relations associated with the dependence of \( y_1 \) and \( y_2 \) on
\( N \). For the width of the reactive window, \( \Omega = y_2 - y_1 \), if we assume that \( \Omega \sim N^\omega \) for large \( N \), then
our data (Fig.4) indicates that \( \omega = 2.1 \pm 0.5 \). For the distance of \( y_2 \) from \( 2/3 \), \( \Delta = 2/3 - y_2 \), if we
assume that \( \Delta \sim N^{\lambda} \) for large \( N \), then our data (Fig.4) indicates that \( \lambda = 2.1 \pm 0.1 \).

4. SIMULATION RESULTS FOR N-RANDOM ADSORPTION MODELS

As mentioned in Sec.3.2, we find true bistability in this model. Results for the van der
Waals type loops in the steady state \([A]\) versus \( y \) are shown in Fig.5 for \( N = 1, 2 \) and 4. The
stable branches can be determined using either a conventional or a constant-coverage
simulation, but the unstable branches were necessarily found using a constant-coverage
simulations. We further checked for bistability by preparing the system slightly above
(below) the unstable branch, and checking that it evolved to the poisoned (reactive) state. For
the larger \( N \), \([A] \) versus \( y \) near the spinodal approximates a vertical line, so precise
determination of \( y_2 \) versus \( N \) is difficult. Thus, instead, we simply ran the constant coverage
simulation for \([A_o] = 0.5\), and show in Table 3 the convergence of the corresponding \( y = y([A_o]) \)
values to \( 2/3 \), as \( N \) increases. If we assume that \( \Delta[A_o] = 2/3 - y[A_o] \sim e^{-\mu N} \), then fitting our data
indicates that \( \mu = \mu[A_o] = 0.46 \pm 0.03 \), for \([A_o] = 0.5 \). This dependence is fundamentally different
from behavior of transition locations in the \( N \)-local adsorption models, and corresponds to
Fig. 4 Scaling analysis of the N-local model simulation results for $\Delta = 2/3 - y_2$ and $\Omega = y_2 - y_1$. 
Fig. 5 "Phase diagram" for the $N$-random models determined by simulation. Plotted is the steady state $A$-coverage, $[A]$, vs. the $A(g)$-impingement probability, $y$. The open symbols indicate the unstable reactive steady state branch. The solid symbols indicate the stable reactive steady state branch, and the line $[A] = 1$ gives the stable $A$-poisoned steady state (common to all $N$).
mean-field-type behavior (see Sec.5). We note that fluctuations in $y$ in the constant-coverage simulations are reduced for large $N$ in the $N$-random model, just as in the $N$-local model. However, we find somewhat stronger finite-size effects in the $N$-random model: $y[A_0]$-values decrease with increasing system size [e.g., by $O(10^3)$ changing from a 500x500 to a 1000x1000 lattice].

Table.3 N-random models. Behavior of $y(A_0)$, for $A_0=0.5$.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$y(A_0=0.5)$</th>
<th>$2/3 \cdot y(A_0=0.5)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.42812</td>
<td>0.23854</td>
</tr>
<tr>
<td>2</td>
<td>0.54784</td>
<td>0.11883</td>
</tr>
<tr>
<td>4</td>
<td>0.62740</td>
<td>0.03926</td>
</tr>
<tr>
<td>8</td>
<td>0.66117</td>
<td>0.00549</td>
</tr>
<tr>
<td>12</td>
<td>0.66581</td>
<td>0.00086</td>
</tr>
<tr>
<td>16</td>
<td>0.666534</td>
<td>0.000133</td>
</tr>
<tr>
<td>20</td>
<td>0.6666434</td>
<td>0.0000233</td>
</tr>
</tbody>
</table>

It is appropriate to comment on why these models display true bistability, rather than a discontinuous $A$-poisoning transition, for all $N$. To this end, one might consider another class of dimer adsorption mechanisms where after the first empty site is selected, one checks $N$ others randomly located within a distance $L$ of the first site. For finite $L$, one again expects to find a discontinuous transition. However, presumably $L$ determines the critical size of a nucleus of the stable poisoned (reactive) state embedded in the metastable reactive (poisoned) state, for impingement rates, $y$, above (below) the transition. Thus as $L$ increases (for fixed $N$), so does the critical size, and thus so does the lifetime of the metastable state.
5. MEAN-FIELD THEORY

We now present a rate equation analysis for both models in the mean-field site-approximation. Here all spatial correlations are neglected, so multisite configuration probabilities simply factorized into products of site probabilities. However the infinite reaction rate, and unusual dimer adsorption mechanism in the N-local model, cause some complications. In this discussion, let A(B) also represent the coverage or concentration of A(B) on the surface, and let E represent the fraction of empty sites. For both species J=A and B, it is convenient to introduce rates for non-reactive (NR) adsorption, \( Y_J(NR) \), and reactive (R) adsorption (adsorption followed by instantaneous reaction), \( Y_J(R) \), as well as the previously discussed total (T) adsorption rates, \( Y_J(T) = Y_J(NR) + Y_J(R) \). Then the rate equations (for infinite reaction rate) have the form\(^{14,15}\)

\[
\frac{dA}{dt} = Y_A(NR) - Y_A(R) = Y_A(NR) + Y_A(NR) - Y_A(T)
\]

\[
\frac{dB}{dt} = Y_B(NR) - Y_B(R) = Y_B(NR) + Y_B(NR) - Y_B(T)
\]

In a steady state, one has \( dA/dt = dB/dt = 0 \) providing a set of coupled nonlinear algebraic equations for A and B (noting that A+B+E=1).

For the \( Y_A \)'s, in both the N-local and N-random adsorption models, we have

\[
Y_A(T) = yE \quad \text{and} \quad Y_A(NR) = yE(1 - B)^4
\]
The first result is exact (as noted previously), and the second simply accounts for the fact that non-reactive A-adsorption requires that none of the four neighbors of the adsorption site be occupied by B (producing an extra factor of \((1-B)^4\) in the site approximation). Next consider the \(Y_B\)'s. In both models, we have

\[
Y_B(T) = 2(1 - y)E(1 - (1 - E)^N).
\]

This expression is exact for N-random adsorption, as noted above. Clearly there are two contributions to the filling of an empty site by B: direct adsorption where the site is selected first by the "bottom atom" in the depositing dimer; and indirect adsorption where the site is selected by the "top atom" in the dimer as a result of searching \(N\) other sites. Clearly, both contributions to \(Y_B(T)\) are equal. However for the \(Y_B(NR)\), behavior is model specific, as detailed below.

5.1 Analysis Of N-Local Adsorption Models

First we consider separately the case \(N=1\) (the ZGB model), where direct and indirect contributions to \(Y_B(NR)\) are equal. Here it has been shown that

\[
Y_B(NR) = 2(1 - y)E^2(1 - A)^3,
\]
which is proportional to the probability of finding an empty site (accommodating the bottom B-atom), surrounded by an empty site (accommodating the top B-atom) and three non-A sites (thus avoiding reaction of the bottom B-atom).

In the N-local model for general N corresponding to some specific number of "shells" (N=4, 8, 12, ..), our chosen search algorithm allows us to sum cumulatively contributions to $Y_B(NR)$ from each shell, but necessarily separating distinct contributions from direct $[\delta Y_B(NRD)]$ and indirect $[\delta Y_B(NRI)]$ adsorption. We thus obtain

$$\delta Y_B(NRD) = (1-y)E[(1-A)^4-B^4], \text{ for the first-shell,}$$

$$= (1-y)EB^4[1-(1-E)^4], \text{ for the second-shell,}$$

$$= (1-y)EB^4[1-(1-E)^4][1-(1-E)^4], \text{ for the third-shell, etc.}$$

The first-shell contribution accounts for the requirement that no first-shell sites can be occupied by A, but also that they cannot all be occupied by B. For second-shell adsorption, all first-shell sites must be occupied by B, and at least one second-shell site must be empty, etc. Similarly, we obtain

$$\delta Y_B(NRI) = (1-y)E(1-A)^3[1-(1-E)^4], \text{ for the first-shell,}$$

$$= (1-y)E(1-E)B^2(1-A)^3[1-(1-E)^4], \text{ for the second-shell,}$$

$$= (1-y)E(1-E)^2B(1-A)^3[1-(1-E)^4], \text{ for the third-shell, etc.}$$
For the first-shell contribution, one requires the indirectly filled site of interest to be empty, one of its four neighbors (the direct adsorption site) to be empty, and the other three not be filled by A (denoted by A' in fig.6). One then sums over all possible states of the other three sites (denoted by * in fig.6) neighboring the direct adsorption site, weighting by the probability that the top atom selects the empty site of interest to fill indirectly. Performing this sum (see Fig.6) yields the above expression, which can also be understood as follows. Pick the site of interest to be filled indirectly. As noted above, one of the four neighbors must be the direct adsorption site, and must be empty, contributing a factor of $4E$; the other neighbors cannot be occupied by A, contributing a factor of $(1-A)^3$. In order for the top B-atom to land, at least one of the neighbors of the direct adsorption site must be empty, contributing a factor $(1-(1-E)^4)$. There is a probability of 1/4 that this neighbor is the site of interest. Contributions to $Y_B$ from indirect filling of other shells can be understood similarly.

Fig.7a shows mean-field predictions for the steady state $[A]$ versus $y$, for three $N$ values, using above expressions for adsorption rates. These predict qualitatively correct behavior, apart from the expected absence of a continuous B-poisoning. The location of the spinodals in the $N=1$ (ZGB), $N=4$, and $N=8$ models are $y_s=0.561012$ (cf. Ref.14), 0.663667, and 0.666629, respectively.

5.2 Analysis Of N-Random Adsorption Models

For dimer adsorption on an infinite lattice, the two B's will land on infinitely separated randomly selected sites. Clearly the probability that either will react is the same, and therefore the direct and indirect contributions to $Y_B$ are equal. The only difference from
Fig. 6 Determination of the first-shell contribution to $\delta Y_B(\text{NRI})$. The **direct** (indirect) adsorption site is the empty site on the right (left). The sum determines the **indirect** B-adsorption rate on the left E-site, accounting for all possible configurations of the * sites. If $m$ of these are E, and thus $3-m$ are A or B, the probability that indirect adsorption occurs on the left E-site is $1/(m+1)$. Here $A'$ means 'not' A.

$$\delta Y_B(\text{NRI}) = 4A'3E^2\sum_{m=0}^{3} \frac{1}{m+1} \binom{3}{m} E^m (1-E)^{3-m}$$
Fig. 7 Mean-field "phase diagrams". Plotted are the steady state A-coverage, $[A]$, vs the A(g)-impingement probability, $y$. (a) $N$-local models for $N=1, 4$ and 8. (b) $N$-random models for $N=1, 2, 4$ and 8.
the total rate is that we must multiply by the probability that there are no A’s on the four nearest neighbors of the adsorbed B. Therefore the non-reactive rate for the B is

\[ Y_b(NR) = 2(1 - y)E(1 - (1 - E)^N)(1 - A)^4. \]

Fig. 7b shows mean-field predictions for the steady state [A] versus y, for three N values, using above expressions for adsorption rates. Qualitatively correct behavior is predicted. The values for the spinodals are \( y_s = 0.57691, 0.64253, 0.66437 \) and 0.6666433 for N=1, 2, 4 and 8 respectively.

5.3 Asymptotic Behavior for Large N

Now we will show that mean-field predictions for the spinodal location (in both models) has a deviation from 2/3 that decreases exponentially with N. It is convenient to analyze the behavior of y for fixed A=A_0, with corresponding E=E_0. Since \( Y_A(T) = Y_B(T) \), one has

\[ y = \frac{2}{3}\left[ 1 - \frac{1}{3}(1 - E_0)^N \right] \]

for large N and 0<E_0<1. Then, solving for \( \Delta = 2/3 - y \), we have \( \Delta = e^{-\mu N} \), as \( N \to \infty \), where \( \mu = -\ln(1-E_0) > 0 \). Thus we have exponential decay provided 0<E_0<1, which presumably applies to the spinodal. Furthermore, for the N-random model, we can obtain simply an exact expression for the decay rate. In the steady state here, we have
\[
\frac{dA}{dt} = yE(A + E)^4 + 2(1 - y)E(1 - (1 - E)^N)((1 - A)^4 - 1) = 0.
\]

Letting \(N \to \infty\), and \(y \to 2/3\), we have for the steady state,

\[
(A_o + E_o)^4 = 1 - (1 - A_o)
\]

which has a solution \(E_o\), satisfying \(0 < E_o < 1\), for any \(A_o\) between zero and one. Solving for \(1 - E_o\), we obtain

\[
\mu = -\ln \left[ 1 + A_o - \left(1 - (1 - A_o)^4\right)^{1/4} \right]
\]

The maximum decay rate, corresponding to the spinodal, occurs at \(A_o = 1 - 2^{-1/4} = 0.159\) yielding \(\mu = -\ln(2 - 2^{-3/4}) = 1.145\).

6. CONCLUSIONS

We have provided a detailed analysis of the influence of the dimer adsorption mechanism on reactivity in the diffusionless monomer-dimer surface reaction model. First, we let the dimer sample \(N\) sites in a local neighborhood of a randomly selected empty site in order to find a second empty site allowing adsorption. We find that the width of the reactive window
between poisoning transitions decreases continuously like $N^{2.140.5}$, and shifts towards the stoichiometric value of the relative impingement rates ($y=2/3$) like $N^{2.140.1}$. Instead, letting the dimer sample $N$ other randomly chosen sites produces true bistability. Now the spinodal approaches $y=2/3$ exponentially, corresponding to mean-field-type behavior.

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REFERENCES


CHAPTER 3. HYBRID TREATMENT OF SPATIO-TEMPORAL BEHAVIOR IN SURFACE REACTIONS WITH COEXISTING IMMOBILE AND HIGHLY MOBILE REACTANTS


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ABSTRACT

For surface reactions on single-crystal substrates which involve highly mobile adspecies, there is a vast separation in natural time and length scales. Adspecies hop rates can be many orders of magnitude larger than rates for other processes. Strong spatial correlations or ordering can exist on the atomic scale, while spatial pattern formation occurs on a macroscopic scale. An efficient analysis of such systems is provided by a "hybrid treatment" which we apply here to the monomer-dimer surface reaction model in the case of coexisting immobile dimer adspecies and highly mobile monomer adspecies. Specifically, we combine a mean-field treatment of the "randomized" mobile adspecies, and a lattice-gas description of the immobile adspecies. Monte-Carlo simulations then reveal bistability and "critical" bifurcation phenomena, while precisely accounting for the influence of correlations in the immobile adspecies distribution. A corresponding analysis of the evolution of macroscopic spatial inhomogeneities is achieved through parallel simulation of the distributed
macropscopic points with distinct correlated states and adspecies coverages. These simulations are appropriately coupled to describe diffusive mass transport of the mobile adspecies. In this way, we examine for this model the propagation and structure of chemical waves, corresponding to interface between bistable reactive states, and thereby determine the relative stability of these states.

1. INTRODUCTION

The interplay between non-linear chemical reaction kinetics and the diffusion of reactants can produce a rich variety of spatial pattern formation. Traditionally these phenomena are described by mean-field (MF) reaction-diffusion equations which ignore any spatial correlations or ordering in the distribution of reactants. For surface reactions on single crystal substrates, this treatment is not strictly justified (even for spatially uniform states) since strong correlations are typically produced either by adspecies interactions, or by the limited mobility of some reactants. Appropriate treatment of these correlations could potentially be provided by lattice-gas (LG) modeling. However a basic obstacle is that in many fundamental reactions, including $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$ and $\text{CO} + \text{NO} \rightarrow \text{CO}_2 + \frac{1}{2} \text{N}_2$, the surface hop rates for the most mobile adspecies (CO and NO) are many orders of magnitude higher than the rates for other processes [adsorption, desorption, reaction, and hopping of relatively immobile adsorbed O]. This great separation of time scales makes direct LG simulation difficult. Perhaps even more problematic is the fact that these large hop rates establish spatial patterns on a macroscopic length scale, which coexist with ordering on the vastly shorter atomic length scale of the spatial correlations. Both of these phenomena must be described simultaneously. [For the systems of interest here, there are just these two far-
separated length scales, but it is also possible for surface reactions to exhibit turbulence, where one has a continuum of length scales.]

To efficiently analyze the above type of systems, we adopt a “hybrid treatment” which involves a full LG description for the time-evolution of the distribution of any (relatively) immobile adspecies, together with a local-equilibrium description of any highly mobile adspecies. Specifically, kinetic Monte-Carlo simulation is used to describe the immobile adspecies, and for the case of negligible adspecies interactions considered here, a standard MF treatment is used to describe the highly mobile adspecies. However, if adspecies interactions are significant, a more sophisticated treatment is required to account for correlations in the distribution of the locally-equilibrated mobile adspecies. We note that hybrid treatments of surface reactions have been implemented previously. However, they have not been applied to analyze the basic features of bistability and bifurcations in spatially homogeneous systems. Furthermore, they have not been extended to describe the evolution of macroscopic spatial inhomogeneities. To this end, we have developed a novel technique to analyze such phenomena within a hybrid formalism. This involves parallel simulation of macroscopically separated points with distinct local adspecies coverages, together with incorporation of coupling between these simulations to describe the diffusive mass transport of the highly mobile adspecies.

In this contribution, we analyze a generic monomer-dimer surface reaction model, described in Sec.2, in the limiting regime of highly mobile monomer adspecies and immobile dimer adspecies. We implement a hybrid treatment using a MF description of the highly mobile locally equilibrated species, and a LG description for the immobile species. Monte-
Carlo simulations, described in Sec.3, reveal MF-type bistability and bifurcation behavior, but with some significant modifications due to the influence of correlations in the distribution of immobile adspecies. In Sec.4, we implement the parallel simulation procedure mentioned above to analyze the propagation and structure of chemical waves, corresponding to the interface between bistable reactive states, thus allowing determination of the relative stability of these states. MF-type "dynamic-cluster" approximations for the distribution of immobile adspecies are also shown to provide accurate descriptions of hybrid model behavior (see Appendix A).

2. MODEL DESCRIPTION

We first describe a generic LG model for the monomer-dimer (or A+B₂) surface reaction. This model mimics the oxidation of CO on single crystal surfaces, with A corresponding to the highly mobile CO, and B to the relatively immobile O. Below (g) denotes the gas phase, (ad) denotes the adsorbed phase, and E denotes an empty surface site. Then the reaction model includes the following mechanistic steps: (i) A(g) impinges on the surface at rate y_A (per site), adsorbing if a randomly selected site is empty; (ii) B₂(g) impinges randomly on the surface at rate y_B (per site), adsorbing if both sites in a randomly selected adjacent pair are empty; (iii) each pair of A(ad) and B(ad) on adjacent sites reacts at rate k, forming AB(g), which then desorbs leaving an adjacent empty pair; (iv) each A(ad) can spontaneously desorb at rate d, leaving an empty site; (v) B(ad) is assumed to be immobile, but A(ad) attempts to hop to randomly selected adjacent sites at rate h, the hop being successful only if the selected
site is empty. Implicitly, the above prescription of rates ignores adspecies interactions.

Schematically, one writes

\[
A(g) + E \rightarrow A(\text{ad}) \\
B_2(g) + 2E \rightarrow 2B(\text{ad}) \\
A(\text{ad}) + B(\text{ad}) \rightarrow AB(g) + 2E \\
A(\text{ad}) \rightarrow A(g) + E
\]

Here we normalize impingement rates so that \(y_A + y_B = 1\), which sets the time scale in the model, and also set \(y = y_A\). We also choose the reaction rate \(k = 1\), but other (non-vanishing) values produce qualitatively similar behavior. We consider only a square lattice of adsorption sites, and focus on behavior in the limit of infinite system size. While our simulation studies are performed on finite systems with periodic boundary conditions, we check that finite-size effects are negligible. (The only exception is in the finite-size scaling analysis in Sec.3.2, which exploits finite-size effects.)

From previous studies of this LG model for \(d = 0\) (no A-desorption) with both finite \(k\) and infinite \(k\) (instantaneous reaction), one finds a stable reactive steady state only for a range \(y_1 < y < y_2\). There is a continuous transition to a B-poisoned "adsorbing" state at \(y = y_1\), and a discontinuous transition to an A-poisoned "adsorbing" state at \(y = y_2\). Also, the stable reactive steady state has a metastable extension above \(y_2\), up to a spinodal point \(y = y_s\). For \(h = 0\) [immobile \(A(\text{ad})\)], it has been shown that \(y_1 = 0.391^{11}, y_2 = 0.5256^9, \) and \(y_s = 0.528^{12}\) for infinite \(k\) (instantaneous reaction), and \(y_1 = 0.365^{13}, y_2 = 0.432^{12}, \) and \(y_s = 0.437^{12}\) when \(k = 1\). Introducing diffusion of \(A(\text{ad})\) (so now \(h > 0\)) has little effect on the B-poisoning transition\(^{14,15}\). However
it is expected to greatly enhance metastability of the reactive state for $y > y_2$, and in fact to increase the width of the metastable window $\Delta y = y_s - y_2$. As a result, most simulation estimates of $y_2$ for $h > 0$ have been corrupted since the system tends to become trapped in this metastable reactive state. (See Ref. 15.) This difficulty can be avoided by using the "constant-coverage ensemble" simulation technique, which we have applied here to the above LG model for the case $k = 1$ (and $d = 0$) to show that $y_2 = 0.4320, 0.4284, 0.4247, 0.4234$, for $h = 0, 1, 2, 4$, respectively (cf. Ref. 15).

If $d > 0$, then clearly there is no longer a trivial adsorbing A-poisoned state. Nonetheless, it has been shown that a discontinuous transition, between a "highly reactive" state, and a "low reactivity near-A-poisoned" state, persists for a range of $d > 0$. This discontinuous transition disappears at a "critical value" of $d = d_c > 0^\text{5,6,7,17}$. In this paper, we are interested in behavior of the above model in the regime of very large $h$. This is motivated by the observation that the hop rate for CO is many orders of magnitude larger than the other rates in typical CO-oxidation reactions. We attempt to determine behavior in this regime directly with a "hybrid model" for behavior of the full LG model as $h \to \infty$. Here we assume that, due to very rapid diffusion, A(ad) is distributed randomly on the non-B(ad) sites at all times. Shortcomings of this assumption is discussed below. Thus in the hybrid model for a (macroscopically) spatially uniform system, one tracks the number, $N_B$, and location of all B(ad) on the square lattice of adsorption sites, but only tracks the number, $N_A$, of A(ad). The hierarchic rate equations for this model are described in Appendix A.

Simulation of this model on a (large) finite lattice of $N$ sites is similar to that of the full LG model above. At each Monte-Carlo step, as usual, one randomly selects between
adsorption, reaction, etc., with weights determined by the relative rates for these processes.

When deciding whether to adsorb or desorb A, or to react a B(ad) with an A(ad), it is necessary to decide whether a chosen non-B(ad) site is occupied by one of the randomly distributed A(ad). We say that such a site is occupied by A(ad) with probability \( p = N_a/N_z \), where \( N_z = N - N_B \) denotes the total number of non-B(ad) sites. (Fluctuations in ‘p’ are small for a large system). Thus if it is decided to attempt A-adsorption (A-desorption) at a selected non-B(ad) site, such adsorption (desorption) is implemented with probability \( 1-p \) (\( p \)), measuring the probability that the site is empty (occupied by A), and then \( N_a \) is incremented by +1 (-1). Reaction is treated similarly, if successful requiring \( N_a \) to be incremented by -1, \( N_B \) by -1, and \( N_z \) by +1. Of course, B-adsorption requires \( N_B \) be incremented by +2, and \( N_z \) by -2.

It should be noted that this hybrid model assumes a uniform distribution of A(ad) on all non-B(ad) sites, even if these sites are topologically disconnected by B(ad)-regions. For the full LG model, even in the limit of high mobility, there would be fluctuations in A(ad) coverages between such disconnected regions. Thus our hybrid model cannot precisely describe the \( h \to \infty \) limit of the above LG model. However we have no reason to expect that the influence of such fluctuations is large.

As noted above, we extend our analysis to systems with spatial inhomogeneity on a macroscopic scale determined by the large diffusion rate of A(ad). Our approach is analogous to the treatment of MF reaction-diffusion (partial differential) equations by the "method of lines", where space is discretized into a set macroscopic points. In the MF treatment, the evolution of coverages at each such point is determined by the appropriate MF rate equations,
augmented by a contribution to diffusive flux between adjacent points (which is driven by macroscopic spatial variations in the coverages). However, in the hybrid model, instead of integrating a simple set of MF rate equations at each such macroscopic point, one must perform a separate simulation to describe exactly the distinct local coverages and correlated configurations. Simulations at these individual macroscopic points must be appropriately coupled to describe macroscopic diffusive transport of $A$. This is indicated schematically in Fig. 1.

In the traditional "hydrodynamic" view, description of macroscopic diffusive transport requires determination of the non-trivial collective (or chemical) diffusion coefficient, $D_A$, for the non-equilibrium state associated with each macroscopic point. The validity of the "hydrodynamic" description of mass transport in the type of LG surface reaction models considered here, and the existence (and determination) of associated non-trivial collective diffusion coefficients, has received little attention. For the above LG model, one can however say that $D_A$ scales like $a^3h$, where 'a' denotes the lattice constant. In this work, for simplicity, we implement the simplest description where diffusive transport is described by a constant $D_A$. However we also consider a modified description of transport, which accounts for the influence of $B(ad)$ on the diffusion of $A(ad)$.

3. KINETICS AND STEADY STATES FOR SPATIALLY UNIFORM SYSTEMS

3.1 General Features Of The Phase Diagram And Kinetics

First we describe simulation results for the steady-state behavior of the hybrid model. Fig. 2 shows the variation of the coverage, $\theta_A$, of $A(ad)$ with $y$, for various $d$. Here we choose
Fig. 1 Schematic of parallel hybrid simulation of generally distinct states of macroscopic points, $i$, distributed across the front of a propagating chemical wave separating states $\alpha$ and $\beta$. Non-B(ad) sites, $\_$, are occupied by A(ad) with probability determined by the local coverage, $\theta_A^i$. Simulations are coupled by adjusting $\theta_A^i$ to describe diffusive transport of A(ad).
Fig. 2 Steady-state $\theta_A$ versus impingement rate, $y$, for several values of $d$. For $d < cl_c = 0.14$, there is bistability. The unstable branches are distinguished by the open plot symbols.

These simulations (both standard and CC) were run on 200x200 lattices for 10000-40000 Monte Carlo steps (MCS).
\( \theta_A \) (instead of \( \theta_B \)) only by convention. For \( d < d_c = 0.14 \), one finds bistability, i.e., a range of \( y \) where a stable low-\( \theta_A \) state (\( \beta \)) of high reactivity coexists with a stable high-\( \theta_A \) state (\( \alpha \)) of low reactivity. The state \( \alpha \) is an A-poisoned “adsorbing” state for \( d = 0 \). To test for the existence of true bistability, we have checked that if the one perturbs the system from the unstable state by slightly increasing (decreasing) \( \theta_A \), it will evolve to the stable state \( \alpha \) (\( \beta \)). See Fig. 3. The states \( \alpha \) and \( \beta \) are joined at their spinodal endpoints by an unstable steady-state branch to form a Van-der-Waals type loop\(^5\). For \( d > d_c \), bistability disappears and there is a unique stable steady state for all \( y \). Thus \( d = d_c \) corresponds to a cusp bifurcation\(^7\), and is the non-equilibrium analogue of a critical point.

Conventional simulations, as described in Sec. 2, allow analysis of the stable steady-states, but not unstable states. However, analysis of the non-trivial unstable steady-states (as well as stable steady-states) is possible utilizing a “constant-coverage (CC) ensemble” approach\(^9\). This CC approach has previously provided an alternative to other techniques, but in the analysis of unstable states, it is an indispensable tool. The idea is simply to run the simulation maintaining a fixed value of \( \theta_A \), say, \( \theta_A^* \). As usual, one randomly selects between attempting adsorption, desorption, and reaction events with the appropriate weights. However, now when adsorption is attempted, rather than selecting A with probability \( y \), or \( B_2 \) with probability \( 1 - y \), one attempts to deposit A if \( \theta_A < \theta_A^* \), or \( B_2 \) if \( \theta_A > \theta_A^* \). Then the asymptotic fraction of attempts to deposit A gives the corresponding value of \( y \). In this way, we can map out both the stable and unstable steady-state branches. We have checked that
Fig. 3 “Bistability kinetics” of the spatially uniform system. Plotted is $\theta_A$ versus time for initial states slightly above (below) the unstable steady state branch. The inset figure is a schematic of this evolution.
finite-size effects are insignificant for the 200x200 site lattices used here, and that CC and conventional simulations give the same results for the stable steady-states.

One should in fact expect the occurrence of bistability in the hybrid model for $d<d_c$ (as opposed to a discontinuous transition between $\alpha$ and $\beta$ states, observed in LG models for $h<\infty$ and $d<d_c$). We have already noted that metastability increases in the LG model with increasing $h$, and this naturally produces bistability as $h\to\infty$. A more complete understanding of behavior in the LG model with increasing $h$ comes from considering associated nucleation phenomena. Slightly above (below) the discontinuous transition, the area of the critical nucleus required to trigger the formation of the stable $\alpha$ ($\beta$) state from a metastable $\beta$ ($\alpha$) background is expected to scale linearly with $h$. Thus nucleation in the $h\to\infty$ regime requires macroscopic fluctuations, and so bistability is established.

Another feature of the phase diagram in the hybrid model is the continuous B-poisoning transition. This transition occurs at $y=y_1=0.3775$ when $d=0$. It has been found for the LG model with $d=h=0$ that this transition falls within the university class of Reggeon field theory and directed percolation, and the same appears to be true for the hybrid model. See Appendix B for a complete discussion.

It is possible to estimate the "exact behavior" obtained via simulations for the hybrid model by using MF-type "dynamic-cluster" approximations to describe correlations in the distribution of $B(ad)$. These approximations can describe bistability (but not discontinuous transitions), so might be expected to provide a particularly accurate description of hybrid model behavior. We have developed and analyzed the associated rate equations in both the
site and pair\(^{13}\) approximations (see Appendix A). The site approximation neglects all spatial correlations; that is, the distribution of B(ad) on the surface is assumed random. (Recall that the A(ad) are already randomly distributed in this hybrid model.) The site approximation thus corresponds to the standard MF description of the model. However, in the pair approximation, one accounts for correlations in the occupancy of adjacent pairs of sites by B(ad). The phase diagrams in both approximations are shown in Fig.4. Both display bistability for \(d < d_c = 0.14\), but only the pair approximation supports a B-poisoning transition. In fact, apart from behavior near the B-poisoning transition, both the site and pair approximations describe quite well the exact phase diagram.

3.2 The Critical Point

Another fundamental issue for the hybrid model is the characterization of fluctuation behavior in the vicinity of the critical point which occurs at \(d = d_c = 0.14\) and \(\gamma = \gamma_c = 0.55\). We first note that, for a finite system of \(N\) sites, with translational invariance due to periodic boundary conditions, the basic relationship between root-mean-square (RMS) coverage fluctuations for adspecies \(J = A\) or \(B\), and the associated spatial correlations is

\[
\Delta_j = \left( \langle \theta_j - \langle \theta_j \rangle \rangle^2 \right)^{1/2} = \left[ \frac{\sum_{l,l'} C_{jl,l'} (l,l')}{N^2} \right]^{1/2}.
\]

Here \(C_{jl,l'} (l,l')\) is the species \(J\) pair-correlation function for sites \(l\) and \(l'\), and again \(N\) is the size (number of sites) of the system. See Appendix C for a derivation. To elucidate the
Fig. 4 Steady-state $\theta_A$ versus $y$, from: (a) the site approximation; (b) the pair approximation (with the B-poisoning transition at $y=0.23$). Apart from the B-poisoning transition there, is excellent quantitative agreement between the two approximations and the simulation.
behavior of the fluctuations, consider first MF behavior associated with a random distribution of adspecies in a finite system. Here we have \( C_j \left( \frac{l}{L} \right) = \left( \langle \theta_j \rangle \right) (1 - \langle \theta_j \rangle) \delta_{lL} \) and consequently that \( \Delta_j = N^{-1/2} \left[ \left( \langle \theta_j \rangle (1 - \langle \theta_j \rangle) \right) \right]^{1/2} \). So we naturally consider

\[
F_j = \frac{N^{1/2} \Delta_j}{\left[ \left( \langle \theta_j \rangle (1 - \langle \theta_j \rangle) \right) \right]^{1/2}}
\] (2)

which is identically unity in the MF case.

In Fig.5, we show \( F_A \) and \( F_B \) versus \( d \), for fixed \( y=0.55 \) close to the critical point, and for systems of different linear sizes \( L \) (i.e., \( L \times L = N \)). These quantities display dramatic maxima which occur in the vicinity of the critical point \( d=d_c=0.14 \). Thus behavior more resembles that of a "fluctuation-dominated" critical point in equilibrium theory or in a LG reaction model, rather than MF behavior. In a more comprehensive analysis, for each fixed \( L \), we have found the maximum of \( F_j \) as a function of \( y \) and \( d \), thus locating the finite size estimate, \( (y_c(L), d_c(L)) \), of the critical point location, \( (y_c, d_c) \). This allows a finite-size-scaling analysis to obtain an estimate of the infinite lattice critical point. Here one assumes\(^7\) that \( d_c(L) \) scales with system size as

\[
d_c(L) - d_c = aL^{-\nu}\,.
\] (3)
Fig. 5 Normalized RMS coverage fluctuations, $F_J$, versus $d$, for $y=0.55$, in finite systems of various sizes, $N$: (a) $J=A$; (b) $J=B$. Dramatic maxima are found for $d=d_c$, suggesting that the critical point in the hybrid model is a fluctuation-dominated critical point.
where $v$ is the correlation-length critical exponent. In Fig. 6, we plot $d_c(L)$ against $1/L$. The points for the larger sizes seem to fall on a straight line suggesting that $v = 1$ as for the Ising model in two dimensions. This analysis gives an estimate of $d_c = 0.1405 \pm 0.001$. We attempted a similar analysis to determine $y_c$. The values of $y_c(L)$ saturated too quickly to be fit by a form like (3), but lead to an estimate $y_c = 0.5470 \pm 0.0002$. It is appropriate here to compare these results with the MF theory (Table 1). The critical values of $d_c$ in the MF theories are virtually indistinguishable from the above estimate, although more significant differences are evident in the steady-state values of the coverages.

Table 1  Comparison of critical points for the MF theories and the simulation. Values of $d_c$ and $y_c$ are equal within the errors of our finite-size-scaling analysis for the simulation.

<table>
<thead>
<tr>
<th></th>
<th>$d_c$</th>
<th>$y_c$</th>
<th>$\theta_A^c$</th>
<th>$\theta_B^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>simulation</td>
<td>0.1405</td>
<td>0.5470</td>
<td>0.433</td>
<td>0.128</td>
</tr>
<tr>
<td>pair</td>
<td>0.14160</td>
<td>0.54783</td>
<td>0.42510</td>
<td>0.1297</td>
</tr>
<tr>
<td>site</td>
<td>0.14160</td>
<td>0.54783</td>
<td>0.43570</td>
<td>0.1081</td>
</tr>
</tbody>
</table>

One can also perform a more complete analysis of higher order cumulants of the distribution of (fluctuating) coverages. An assessment of the deviation from Gaussian fluctuations is provided by the variation from zero

$$\text{of} U_L = \left[ \left( \langle \theta_j^4 \rangle - 4 \langle \theta_j^2 \rangle \langle \theta_j^2 \rangle - 3 \langle \theta_j^2 \rangle^2 + 12 \langle \theta_j^2 \rangle (\theta_j)^2 - 6 (\theta_j)^4 \right) \right] \left( 3 \Delta_j^2 \right).$$

(4)
Fig. 6 Finite-size-scaling analysis to locate $d_c = \lim_{L \to \infty} d_c(L)$. Results suggest that $d_c = 0.1405 \pm 0.001$. 
In fact, $U_c$ should be maximized at the critical point and take a value of 0.618 if Ising universality applies, as shown\(^7\) for the LG monomer-dimer reaction with $k = \infty$ and $h=0$. We find a maximum of $0.35 \pm 0.05$ at the critical point for $J=A$ using $L=10$, 20 and 40 (and a lower value for $J=B$). Uncertainty in our statistics precludes definitive conclusion of a deviation from Ising universality.

4. EVOLUTION OF MACROSCOPIC SPATIAL INHOMOGENEITIES

4.1 General Formalism

We now consider the description of macroscopic spatial phenomena within the hybrid model. To elucidate these phenomena, first consider behavior of the full LG model in the regime where the hop rate, $h$, of the highly mobile species, $A(ad)$, is large enough to achieve local equilibration, and to justify the use of a local MF treatment $A(ad)$. However, even in this case, there can be variations in adspecies coverages on a macroscopic length scale\(^2\) which is of the order of $\alpha^{1/2}/\kappa^{1/2}$ or $D_A^{1/2}/\kappa$. Here $\kappa$ denotes an effective rate constant for the overall reaction, ‘$\alpha$’ denotes the lattice constant, and $D_A$ the chemical diffusion coefficient (as previously). It is thus spatial variations on a macroscopic length scale of order $D_A^{1/2}$ which we consider below for the hybrid model.

In the standard “hydrodynamic picture”, the diffusive flux, $J_A$, of $A(ad)$ is determined from the collective diffusion coefficient\(^1\), $D_A$, via the form $J_A = -D_A \nabla \Theta_A$. In general, $D_A$ depends non-trivially on the local state of the system, however typically it is taken as constant. Thus, we adopt this simplification in our treatment of chemical waves in the hybrid
model. However, we also consider one alternative description of transport which falls outside the above general picture. This alternative is motivated by the observation that the above choice of $J_A$ does not guarantee that $\theta_A + \theta_B \leq 1$ at each macroscopic point\cite{16}. To address this shortcoming, we must assess the influence of the presence of $B(\text{ad})$ on $A(\text{ad})$-diffusion. A "mean-field" estimate of this influence leads us to consider the choice

$$J_A = -D_A \nabla \theta_A + D_A (\theta_B \nabla \theta_A - \theta_A \nabla \theta_B),$$

which enforces the condition $\theta_A + \theta_B \leq 1$. The derivation of this result in Appendix D also indicates that correlations in the $B(\text{ad})$-distribution would modify $J_A$, but no simple treatment of these effects is possible. An alternative approach would be to analyze the diffusion of $A(\text{ad})$ on percolating clusters of non-$B(\text{ad})$ sites, using ideas from transport in disordered media. However this is somewhat inconsistent with the imposition in the hybrid model of equal $A(\text{ad})$-coverages on disconnected clusters on non-$B(\text{ad})$ sites. Consequently we only treat diffusion by the simpler prescriptions above.

For hybrid model parameters in the bistable region, it is possible to consider propagation of chemical waves corresponding to the motion of the interface between stable states $\alpha$ and $\beta$. From above, the characteristic length for such waves is of the order $D_A^{1/2}/\kappa$, and it readily follows that the characteristic velocity is of the order $(\kappa D_A)^{1/2}$. Here we consider only planar chemical waves traveling in the $x$-direction, say, and simulate in parallel the generally distinct local states of the system at discrete macroscopic points, $i = ..., -1, 0, 1, ...$ with positions $x = i \delta D_A^{1/2}$; here typically $\delta$ is chosen around 0.1. We denote the associated local coverages of $A(\text{ad})$ by $\theta_A^i$. To describe the effects of macroscopic diffusion, we must
incorporate diffusive mass flow of $A$ between neighboring macroscopic points. Therefore, in addition to running the hybrid model simulations independently at each point, at small time increments, $\Delta t$, we make an additional adjustment of the $\theta^i_A$, via $\delta \theta^i_A = -\nabla \cdot I^i_A \Delta t$, to account for this mass flow. Finally, we note that in order to reduce the number of macroscopic points (and thus the number of simulations we have to run in parallel) required for an accurate description of spatial variations, we use higher order approximations to derivatives in calculating mass flow. For example, when $I_A = -D_A \nabla \theta_A$, we use

$$-\nabla \cdot I^i_A = D_A \nabla^2 \theta^i_A = \frac{-\theta^{i+2}_A + 16\theta^{i+1}_A - 30\theta^{i}_A + 16\theta^{i-1}_A - \theta^{i-2}_A}{128}.$$  \hspace{1cm} (5)$$

Typical number of macroscopic points used was 100-300 and the lattices used for each macroscopic point had from 100x100 to 200x200 sites.

It is also possible to analyze macroscopic spatial phenomena using the MF-type "dynamic cluster" approximations described in Appendix A. Now $\theta_A$ and $\theta_B$, as well as probabilities of larger clusters of sites, depend on (macroscopic) position, and one must simply augment the $d\theta_A/dt$ equation with a diffusive term, $-\nabla \cdot I_A$. (Recall that $A(ad)$ is locally randomized, and that $B(ad)$ does not diffuse.) We also present the results of such analyses below.

4.2 Chemical Wave Velocity And Equistability Points

First, for $d=0$, we determine the variation in the propagation velocity, $V$, of the interface between states $\alpha$ and $\beta$, as $y$ scans the bistable region. Fig.7 shows results from "parallel simulations" for both the standard and modified choices of $I_A$. The results reveal the
Fig. 7 Propagation velocity of chemical waves, $V$, versus $y$, in the bistable region, for $d=0$: (a) standard diffusion, $y_e=0.4404$; (b) modified diffusion, $y_e=0.4185$. The velocity goes to zero at $y=y_e$, the equistability point.
existence of a point \( y = y_c \) where the propagation velocity vanishes. For \( y < y_c \), state \( \beta \) displaces \( \alpha \) (\( V > 0 \)) and thus \( \alpha \) is "more stable", but for \( y > y_c \), state \( \alpha \) displaces \( \beta \) (\( V < 0 \)) and thus \( \beta \) is "more stable". Thus \( y = y_c \) is the "equistability point" for states \( \alpha \) and \( \beta \). This is where one would perform a "kinetic Maxwell construction" on the Van-der-Waals type loops in Fig.2 (by analogy with thermodynamic systems). The feature that the location of the equistability point can depend on the description of diffusive mass transport was already recognized from MF reaction-diffusion equation studies. We performed a corresponding analysis using the site- and pair-approximations. Table 2 shows close agreement between predictions of these approximations and the "exact" simulation results. This is perhaps not surprising given the success of these approximations in describing behavior of the hybrid model (away from the B-poisoning transition).

Table 2 Comparison of equistability points, \( y_c \), for the MF theories and simulation.

Incorporation of B(ad) correlations in the pair approximation produce particularly precise results.

<table>
<thead>
<tr>
<th></th>
<th>comparison of equistability points for ( d = 0 )</th>
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<tbody>
<tr>
<td></td>
<td>simulation</td>
</tr>
<tr>
<td>modified</td>
<td>0.4185</td>
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</tbody>
</table>
It is appropriate to compare these results with our estimates of behavior in the full LG model (with immobile B(ad), and mobile A(ad) with hop rate h), in the limit as \( h \rightarrow \infty \). In this LG model, we estimated that the discontinuous transition shifts to about \( y = 0.423 \), as \( h \rightarrow \infty \) (see Sec. 2). Since this discontinuous transition corresponds to the equistability point in the hybrid model, comparison with Table 2 suggests that the modified description of diffusive transport of A(ad) better describes limiting behavior in the LG model.

Finally, we consider behavior at the equistability point for states \( \alpha \) and \( \beta \) for the range \( 0 < d < d_c \). The variation of \( y_e \) over this range of d is shown in Table 3. Fig. 8 shows the corresponding \( \theta_A \)-concentration profile of the stationary interface or "kink" between states \( \alpha \) and \( \beta \). This kink clearly smears out as \( d \rightarrow d_c \). In order to quantify this "critical" roughening, we define an interface width, \( \omega \), as the dispersion of \( \frac{\partial \theta_A}{\partial x} \). The results, also shown in Table 3, support the expectation that \( \omega \rightarrow \infty \), as \( d \rightarrow d_c \), although it is difficult for us to quantify the nature of this divergence.

5. CONCLUSIONS

In summary, we have proposed a hybrid treatment for surface reactions where immobile and highly mobile reactants coexist. We implemented a LG description of the immobile adspecies (thus describing spatial correlations in their distribution), and a MF description of the highly mobile adspecies. In the cases considered here, the high mobility produced a well-mixed locally equilibrated adlayer of the mobile adspecies, quenching fluctuations, and inducing very strong metastability (and hysteresis) in the full LG model. This was reflected
Table 3 Simulation results for $y_c$, $\omega$, and the upper and lower spinodals, $y_{u^*}$, for $0 \leq d \leq d_c$: (a) standard diffusion; (b) modified diffusion.

<table>
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<th>(a) Standard Diffusion Treatment</th>
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<th>(b) Modified Diffusion Treatment</th>
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<tr>
<td>$d$</td>
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Fig. 8 Chemical wave profiles at $y = y_e$ for various $d$. Note the increasing width of the wave profile as $d \rightarrow d_c$: (a) standard diffusion; (b) modified diffusion.
by the presence of bistability in the hybrid model. Our analysis of the monomer-dimer \((A+B_2)\) surface reaction, with highly mobile \(A(ad)\) and immobile \(B(ad)\), has shown that spatial correlations in the \(B(ad)\)-distribution do not significantly modify features of the MF phase diagram (for a system with macroscopic spatial homogeneity), such as bistability and cusp bifurcations. However detailed fluctuation behavior in the vicinity of such bifurcations, and the occurrence of continuous poisoning transitions, is quite distinct from MF behavior. We also show how to treat macroscopic spatial inhomogeneities, such as chemical waves, within this hybrid formalism. This allows, e.g., determination of the equistability point in the bistable region (the kinetic analogue of Maxwell’s construction). The associated novel parallel simulation procedure for incorporating atomic scale correlations into the analysis of macroscopic spatial phenomena is quite general, well suited to parallel computer architectures, and effectively limited only by availability of detailed energetic and mechanistic information characterizing atomic reaction processes.

APPENDIX A: HIERARCHIC RATE EQUATIONS AND APPROXIMATIONS

Here we briefly discuss the exact hierachic rate equations for the hybrid model, and describe site- and pair-approximations to these. These hierarchic equations for general LG models describe the evolution of probabilities (or concentrations) for various subconfigurations of sites. In the hybrid model, some simplifications arise due to the feature that the \(A(ad)\) are strictly randomly distributed. For convenience, below we present the probabilities of various configurations by the configurations themselves. Thus one
has $A = \theta_A$, $B = \theta_B$, and $E$, $AB$, $BBA$, $A^B_B^B$, etc. represent the probabilities of an empty site, an A(ad)-B(ad) pair, linear and bent B(ad)-B(ad)-A(ad) triples, etc.

It is instructive to consider first the general LG model for the A+\text{B}_2 reaction, where there are three single site configuration probabilities, $A$, $B$, and $E$, and six distinct pair configurations probabilities, $AA$, $BB$, $EE$, $AB$, $AE$, and $BE$. (Note that by inversion symmetry $BE = EB$, etc.) However, there are also conservation of probability conditions.

$A + B + E = 1$, and $AA + BB + EE + 2AB + 2AE + 2BE = 1$. Also the single site probabilities can be determined from the pair probabilities via the relations $AB + AE + AA = A$, $AB + EB + BB = B$, and $AE + BE + EE = E$. In the hybrid model, further relationships exist.

To see this, introduce a state $Z$ describing a site is not occupied by $B$. Then one has $Z + B = 1$.

$ZZ + 2ZB + BB = 1$, etc. Clearly, a $Z$-site can be either empty, with probability $\frac{E}{Z}$, or occupied by $A$, with probability $\frac{A}{Z}$. Also note that since $A(\text{ad})$ are randomly distributed, one has

\begin{align*}
AA &= ZZ\left(\frac{A}{Z}\right)^2, \\
EE &= ZZ\left(\frac{E}{Z}\right)^2, \\
AB &= ZB\left(\frac{A}{Z}\right) \\
EB &= ZB\left(\frac{E}{Z}\right).
\end{align*} \quad (6)

The above discussion shows that the state of single site and pair configurations in the hybrid model is fully (and conveniently) described by the three independent quantities $A$, $B$, and $ZB$. The exact rate equations for these are
\[
\frac{dA}{dt} = yE - 4kAB - dA, \quad \frac{dB}{dt} = 2yEE - 4kAB, \quad \text{and}
\]
\[
\frac{dBB}{dt} = \frac{(1-y)}{2} \left( EE + 4 \frac{E}{B} + 2BEE \right) - 2k \left( BBA + 2 \frac{A}{B} B \right)
\]

where \( k = 1 \) in our study. The terms on the right hand side simply account for all possible ways to create or destroy the configurations of interest by adsorption, desorption, or reaction.

In the site-approximation, one simply factorizes all configuration probabilities in terms of single site probabilities. This closes the first two equations, and produces the standard MF approximation to the A+B_L G reaction model. In the pair-approximation, these equations are closed by factoring the triplet configuration probabilities as \( IJK = \frac{IJ \cdot JK}{J} \) where \( I, J, K \), are any of \( A, B, Z, E \), and then by applying (6) together with conservation of probability conditions.

APPENDIX B: THE B-POISONING TRANSITION

One feature of the hybrid model, characteristic also of the full LG model, is the appearance of a B-poisoning transition. For \( d=0 \), we determine precisely here the location, \( y=y_1 \), of this transition, as well as the associated critical exponents, and compare with behavior in the corresponding immobile LG model. We utilize an "epidemic analysis", which involves monitoring the evolution of an empty patch embedded in a B-poisoned background\(^{11}\). The quantity of interest is the epidemic survival probability, \( P_s(t) \). That is,
$P_s(t)$ is the probability that at time $t$ the lattice has not completely poisoned with B. For $y<y_1$, the $t\to\infty$ asymptotic survival probability approaches zero exponentially, while for $y>y_1$, it is non-zero. At $y=y_1$, the survival probability is expected to scale like $P_s(t)\sim t^\delta$, as $t\to\infty$. To precisely determine the exponent, $\delta$, it is useful to consider the "local exponent" defined as

$$\delta(t) = \frac{\log[P_s(t)/P_s(t/5)]}{\log(5)}.$$  

(8)

Thus, as $t\to\infty$, the local exponent should approach zero for $y>y_1$, and it should diverge for $y<y_1$. At $y=y_1$ it can be shown that, for large $t$, $\delta(t)=\delta+a/t$. In Fig.9a shows $\delta(t)$ versus $1/t$ for the hybrid model bending downward towards zero for $y=0.378$ (indicating that $y_1<0.378$), and bending upward for $y=0.377$ (indicating that $y_1>0.377$). Therefore we conclude that $y_1=0.3775\pm0.0005$. The data is also consistent with a value of $\delta=0.452$ associated with the universality class of Reggeon field theory. We performed an identical analysis for the immobile LG model with $k=1$ (Fig.9b) indicating that $y_1=0.3645\pm0.0005$ (and $\delta=0.452$).

These results reveal a small but definite difference between the values of $y_1$ for the hybrid and immobile LG models. Since the only difference between these models is the treatment of $A_{(ad)}$, and since $\theta_A$ vanishes at the B-poisoning transition, one might have expected that the values of $y_1$ would be the same. However, we shall see that although $\theta_A$ vanishes at $y=y_1$, the "local concentration", $\theta_A^{loc}=\theta_A/\theta_Z$, of $A_{(ad)}$ on non-B or Z-sites remains finite. We believe this produces the difference in model behavior. From simulations, we find that $\theta_A^{loc}$
Fig. 9 Epidemic analysis results for $\delta(t)$: (a) hybrid model, $y_1 = 0.3775 \pm 0.0005$; (b) immobile model, $y_1 = 0.3645 \pm 0.0005$. 
approaches about 0.127 for the hybrid model, and 0.005 for the immobile model, as $y \to y_1$.

Similarly, in the pair approximation, the location of the B-poisoning transition in the hybrid model of $y_1 = 0.2374$, differs slightly from the immobile LG model value of $y_1 = 0.2340$. We find that the pair approximation estimate of $\theta_A$ approaches about 0.07, as $y \to y_1$, in both models.

APPENDIX C: FLUCTUATIONS IN ADSPECIES COVERAGE

We start by considering the RMS fluctuations in coverage for adspecies $J$ in a translationally invariant surface reaction model on a finite lattice of $N$ sites with periodic boundary conditions. Now introduce a site occupation number $n_l$ which is equal to one if site $l$ is occupied by $J$, and zero otherwise. Then we can write the coverage as $\theta_J = \frac{1}{N} \sum_l n_l$, so

$$\langle \theta_J \rangle = \langle n_l \rangle,$$

for all $l$. The fluctuations are given by

$$\Delta_J^2 = \langle (\theta_J - \langle \theta_J \rangle)^2 \rangle = \left\langle \frac{1}{N^2} \sum_{l<l'} (n_l - \langle n_l \rangle)(n_{l'} - \langle n_{l'} \rangle) \right\rangle$$

$$= \frac{1}{N^2} \sum_{l<l'} (n_l - \langle n_l \rangle)(n_{l'} - \langle n_{l'} \rangle) = \frac{1}{N^2} \sum_{l<l'} C_{ll'}$$

(9)

where $C_{ll'} = \langle n_l n_l' \rangle - \langle \theta_J \rangle^2$ is the species $J$ pair-correlation function.
For a random distribution of adspecies, we have \( \langle n_l n_{l'} \rangle = (\Theta_j)^2 \) for \( l \neq l' \). For \( l = l' \), note that \( n_l^2 = n_l \) so that \( \langle n_l n_l \rangle = (\Theta_j) \). Now the pair-correlation function becomes

\[
C_{ll'}(l, l') = (\Theta_j)(1 - (\Theta_j))\delta_{l l'}.
\]

For \( 1 \leq l \leq N \), that \( n_l = n \), so that \( \Theta = (\theta_j) \). Now the pair-correlation function becomes

\[
\Delta_j^2 = \frac{1}{N^2} \sum_{l,l'} (\Theta_j)(1 - (\Theta_j))\delta_{l l'} = \frac{(\Theta_j)(1 - (\Theta_j))}{N}.
\]

\section*{APPENDIX D: THE DIFFUSIVE FLUX}

For a linear lattice, let \([M_i]\) denote the probability that site \( i \) is occupied by species \( M=A, B, \) or \( E \). Also let \([M_i N_{i+1}]\) denote the probability that site \( i \) is occupied by species \( M \), and site \( i+1 \) is occupied by species \( N \). Then for the one-dimensional A+B₂ LG reaction model where A(ad) has hop rate \( h \), the net diffusive flux of A(ad) from site \( i \) to site \( i+1 \) is given by

\[
J_{i \rightarrow i+1} = h([A_i E_{i+1}] - [E_i A_{i+1}]) = -h([A_{i+1}] - [A_i]) + h([B_i A_{i+1}] - [A_i B_{i+1}]).
\]

where we have used the relations \([A_i E_{i+1}] + [A_i B_{i+1}] + [A_i A_{i+1}] = [A_{i+1}]\) and

\([E_i A_{i+1}] + [B_i A_{i+1}] + [A_i A_{i+1}] = [A_{i+1}]\). Ignoring all spatial correlations (so one can write

\([M_i N_{i+1}]=[M_i][N_{i+1}]\), and defining \(\nabla [M_i]=[M_{i+1}]-[M_i]\), we obtain

\[
J_{i \rightarrow i+1} = -h\nabla [A_i] + h([B_i] \nabla [A_i] - [A_i] \nabla [B_i]).
\]
It is trivial to generalize this analysis to a two-dimensional square lattice. Taking a continuum limit for slowly varying adspecies concentrations, where $a J_{j_{i}j_{i+1}} \rightarrow J_x$, $a^2 h \rightarrow D_A$, and $a^{-1} \Delta \rightarrow \partial / \partial x$, yields the expressions given in Sec.4.1.

ACKNOWLEDGEMENTS

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CHAPTER 4. PERCOLATIVE DIFFUSION OF CO DURING CO-OXIDATION ON Pt(100)


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ABSTRACT

During CO-oxidation on Pt(100), CO diffuses in a "disordered environment" produced by a complex pattern of reconstructed and unreconstructed regions of the substrate. Macroscopic diffusion of CO is only possible on percolating 1x1-regions of the substrate. We analyze spatio-temporal behavior accounting in the simple way for the percolative nature of CO-diffusion in this system. This is done via incorporation into the reaction-diffusion equations of a suitable chemical diffusion coefficient, exploiting ideas from the theory of transport in disordered media. We then consider the propagation of reactive, O-rich pulses into a CO-covered 1x1-background.

I. INTRODUCTION

A rich variety of spatial pattern formation and wave propagation phenomena have been observed recently in surface reactions on single crystal surfaces under ultra-high-vacuum conditions. A characteristic length scale of such features is typically of the order of
10 microns. The reactions studied most intensively have involved either CO-oxidation or NO-reduction [1-3]. The observed spatio-temporal features reflect the rapid diffusion of such adspecies as CO or NO. (Note that any adsorbed O present is relatively immobile.) More specifically, these features depend on the associated chemical or collective diffusion coefficients, which appear in the reaction-diffusion equations describing the evolution of the system. These diffusion coefficients are typically assumed constant, but are in fact highly non-trivial, depending on the locally equilibrated state of the highly mobile adspecies. They describe (and are defined in terms of) the response of the system to macroscopic spatial inhomogeneities [4].

In this contribution, we consider exclusively CO-oxidation on Pt(100) [5]. An important feature of this system is that the clean Pt(100) surface undergoes a “hex”-reconstruction, but significant local coverages of CO (or O) lift this hex-reconstruction to recover a 1x1-structure [6]. In analyzing spatio-temporal behavior in this reaction system, one should regard the highly mobile CO as diffusing in a "disordered environment". This environment is created in part by the other adsorbed CO molecules, as well as coadsorbed and relatively immobile O, but also (and perhaps more importantly) by the complex pattern of reconstructed and unreconstructed regions of the substrate induced by chemisorption. Effectively, CO diffusing on the hex-regions of surface is irreversibly captured upon reaching 1x1-regions. Thus true macroscopic chemical diffusion of CO is only possible via the 1x1-regions of the surface, and in configurations where these regions form a percolating network. (see Fig. 1) Therefore, we conclude that the chemical diffusion coefficient, D_{CO}, for CO can only be non-zero above the percolation threshold for the 1x1-regions. See Fig.1 for a
Fig. 1 Schematic showing (a) localized diffusion of CO, with $D_{CO}=0$, on nonpercolating $1\times1$-regions when $\theta_{1x1}<\theta_c$; (b) macroscopic chemical diffusion of CO, with $D_{CO}>0$, on percolating $1\times1$-regions when $\theta_{1x1}>\theta_c$. Here $\theta_{1x1}$ is the fraction of the substrate in the $1\times1$-state, and $\theta_c$ is the percolation threshold.
schematic, and Ref.[7] for a general discussion of transport in disordered percolating systems. The main focus of this contribution is to make a first attempt to incorporate in a simple way this key feature into reaction-diffusion equation modeling.

Before proceeding, we briefly comment on a two other issues pertaining to chemical diffusion in surface reactions, and specifically to CO-oxidation. As implied above, D_{CO} is influenced not just by the substrate reconstruction, but also by adspecies interactions. In fact, the CO-CO interactions alone induce a strong dependence of D_{CO} on the local coverage of CO [8], an effect which we do not address further here. Another issue arises for reaction systems exhibiting oscillatory kinetics in which there is an associated cyclical nucleation and growth of islands, e.g., of 1x1-CO islands in CO-oxidation on Pt(100). Here one expects to find atomic-scale spatial structure in the form of growing (or shrinking) islands, even in a macroscopically spatially uniform state. The boundaries of such islands are expected to be atomically sharp as a consequence of the strong attractive interactions driving the nucleation process. Sometimes the term “uphill diffusion” is used to describe mass transport to such islands during their growth [9]. Indeed, atomically sharp spatial structures have in fact been observed in recent Field Emission Microscopy and Field Ion Microscopy studies of surface reactions [3], including CO-oxidation on Pt tips [10]. Furthermore, the mean-field reaction-diffusion equation formalism was recently modified to describe the evolution of sharp “phase boundaries”, directly relating their existence to attractive adspecies interactions [11].

However, in our discussion of CO-oxidation on Pt(100), we do not view CO-transport to growing 1x1-CO islands as corresponding to “chemical diffusion”, in the sense defined
above. The atomic scale structure associated with these islands is distinct from the macroscopic spatial variations described by $D_{\text{CO}}$.

In Sec.II, we describe very briefly the model used to analyze CO-oxidation on Pt(100), noting various prescriptions for the reconstruction dynamics, and focusing on our modified treatment of CO-diffusion. We then describe in Sec.III, results for propagation of reactive, O-rich pulses into a CO-covered 1x1-background. Finally, we summarize our findings in Sec.IV.

II. MODEL FOR CO-OXIDATION ON Pt(100)

The basic model for the CO-oxidation kinetics on Pt(100) was developed by Imbihl et al. [5]. One must specify the fraction, $\theta_{1x1}$, of the substrate in the 1x1-state, so then a fraction $\theta_{\text{hex}}=1-\theta_{1x1}$ is in the hex-state. CO can adsorb on both 1x1- and hex-regions, so local coverages, $\theta_{\text{CO}}^{1x1}$ and $\theta_{\text{CO}}^{\text{hex}}$, are specified for each region. O is assumed to adsorb on and populate only the 1x1-regions, so that only a single local coverage, $\theta_{O}^{1x1}$, need be specified. Adsorbed O does not inhibit CO-adsorption, but adsorbed CO does block O-adsorption. One key modification to this adsorption scheme is that O can adsorb at defect sites, even on a CO-covered surface. Other features of the model include CO desorption from both regions, irreversible transfer of CO from the hex- to 1x1-regions via diffusion-mediated trapping, and reaction of adjacent CO and O. Explicit expressions for the rates of these processes, as well as values of associated rate constants, can be found in Ref.5. These are incorporated into our modeling.
It is also necessary incorporate the dynamics of reconstruction into the modeling. The 1\times 1-regions are known to shrink, due to thermally activated reconstruction, when $\theta_{CO}^{1\times 1}$ and $\theta_{O}^{1\times 1}$ drop below certain critical values, $\theta_{CO}^{\text{crit}}$ and $\theta_{O}^{\text{crit}}$, respectively [6]. Thus, one has

$$\frac{d\theta_{1\times 1}}{dt} = -k_{(1-c)}\theta_{1\times 1}, \text{ if } c<1,$$

(1)

where $c = \theta_{CO}^{1\times 1}/\theta_{CO}^{\text{crit}} + \theta_{O}^{1\times 1}/\theta_{O}^{\text{crit}}$ [5]. Imbihl et al. [5] assumed that 1\times 1-regions expand when $\theta_{CO}^{1\times 1}$ reaches some threshold value, $\theta_{CO}^{\text{grow}}$, in a way so as to maintain $\theta_{CO}^{1\times 1}$ at this value. However, recent studies by King and coworkers [12] of the non-linear growth kinetics of 1\times 1-regions suggest that, more precisely,

$$\frac{d\theta_{1\times 1}}{dt} = k_+(\theta_{CO}^{\text{hex}})^n\theta_{\text{hex}}, \text{ if } c>1, \text{ where } n=4.1.$$

(2)

A rather different approach by Andrade et al [13] implements a Ginzburg-Landau formalism based on a suitable Hamiltonian description of the energetics of adsorption and reconstruction. However, such an approach cannot reliably describe the type of far-from-equilibrium kinetics associated with substrate reconstruction in this system [14], as is clear by comparison with Ref. [12]. In this work, we incorporate the prescriptions of Refs. [5] and [12] for the reconstruction dynamics, and compare resulting behavior.

Such models reproduce the oscillatory reaction kinetics observed in experiment, for a restricted range of partial pressures of CO and O, and of substrate temperature, T [2,5]. The steps in the oscillation cycle can be characterized as: (i) O adsorbs at defect sites on a CO-
covered 1x1-surface; (ii) this reduces the CO coverage (due to reaction between adsorbed O and CO), and initiates the 1x1→hex reconstruction; (iii) subsequently most of the adsorbed CO is removed and the O-coverage begins to grow, as do the hex-regions; (iv) eventually the presence of large hex-regions, on which only CO adsorbs, leads to an increase of the CO coverage, corresponding nucleation and growth of 1x1 regions, and finally a return to state (i). Fig. 2 shows an example, relevant to the study in Sec.III, of the oscillatory dynamics using both prescriptions for the reconstruction dynamics. Here the partial pressures and temperature, T=480K, have been chosen such that the system has a long oscillation period, most of which is spent in a predominantly CO-covered 1x1-state. While in this state, adsorbing O slowly reacts away adsorbed CO until the critical coverage is reached, initiating the “rapid” 1x1→hex transformation and recovery to the CO-covered 1x1-state. Note that this rapid dynamics similar to that when system is “excited” just outside the oscillatory regime.

Next we address in more detail the central issue of the description of CO-diffusion in this model. As indicated above, the standard treatments [2,5,13] just include CO-diffusion on 1x1-regions. This is consistent with the feature that CO diffusing on hex-regions is irreversibly trapped by 1x1-regions, and thus cannot undergo macroscopic transport on the hex-regions. However these treatments also set D_{CO} constant, which is not consistent with the fact that chemical diffusion is only possible if the 1x1-regions percolate. In our analysis, we exploit results from the general theory of transport in percolating systems [6,15] to make the simplest consistent choice for D_{CO} of
Fig. 2 Spatially uniform oscillatory reaction kinetics using: (a) the Imbihl prescription with partial pressures, $P_{CO} = 9 \times 10^{-6}$ Torr and $P_{O_2} = 2 \times 10^{-4}$ Torr, and oscillation period $\tau = 15$ sec: (b) the King prescription for the reconstruction dynamics with $P_{CO} = 8 \times 10^{-6}$ Torr, $P_{O_2} = 1.3 \times 10^{-4}$ Torr, and $\tau = 50$ sec. Most of the oscillation cycle is spent in a CO-covered $1\times1$-state.
See Fig. 3. Here \( \theta_c \) is the percolation threshold for the 1x1-regions, \( \mu=1.3 \) is the critical exponent for diffusive transport, and \( D_{CO}^{1x1} \) is the diffusion coefficient for CO on a perfect 1x1-substrate (where \( \theta_{1x1}=1 \)). For a simple model involving irreversible nucleation of islands at random locations, and subsequent growth and coalescence, one expects that \( \theta_c=0.7\text{ML} \) in the regime of "large" characteristic island size [16]. However, for diffusion-mediated nucleation and growth, where there is typically a depletion in the population of nearby islands, \( \theta_c \) can be as high as 0.8\text{ML} [16]. Actually, neither of these analyses apply to the more complicated scenario of reversible growth and shrinkage of islands found in the reaction system, where the value of \( \theta_c \) is rather uncertain. In fact, the above specification (3) is certainly an oversimplification since \( D_{CO} \) really depends on the complete state of the system, which is not determined simply by specifying \( \theta_{1x1} \). However, (3) is a reasonable first approximation.

III. ANALYSIS OF PROPAGATING REACTIVE PULSES

We now perform an analysis of the experimentally observed [5,17] excitation of reactive, O-rich pulses into a quiescent CO-covered 1x1-background. Typically these pulses are generated by "defect regions" at steps. Again we adopt essentially the same model, and
Fig. 3 $\frac{D_{CO}}{D_{CO}^{1\times 1}}$ versus $\theta_{1\times 1}$ for various $\theta_c$. The vertical line indicates the dependence of $\frac{D_{CO}}{D_{CO}^{1\times 1}}$ on $\theta_c$ for fixed $\theta_{1\times 1}$. 
values of all rate parameters, as in Ref.[5], but consider both the prescriptions of Imbihl et al [5], and King and coworkers [12], for the growth of $1\times 1$-regions. We compare behavior produced by the standard choice of constant $D_{\text{CO}}$ with that produced by the form (3), for various $\theta_c$. We choose the surface temperature, $T=480\,\text{K}$, and partial pressures of CO and O, just as in Fig.2, so that the homogeneous system has a long oscillation period most of which is spent in the CO-covered $1\times 1$-state. For our studies of pulse propagation, we take a semi-infinite system with a defect region at the left end of width 0.01cm characterized by enhanced oxygen adsorption rate. After initiating adsorption at $t=0$, the system quickly attains a CO-covered $1\times 1$-state, into which the defect regions excite reactive pulses. Similar behavior is observed if the homogeneous system is not in, but is sufficiently near the oscillatory region, that the system is “excitable” [18,19]. In fact, such systems provide a useful generic paradigm for the behavior observed here. Typical results for concentration profiles, obtained by numerical integration of the reaction-diffusion equations with $D_{\text{CO}}^{1\times 1}=4\times 10^{-4}\,\text{cm}^2/\text{s}$, are shown in Fig.4.

First, we provide some general remarks about the observed pulse propagation. At the front of the pulse, CO diffuses to the left, reducing $\theta_{\text{CO}}^{1\times 1}$ in the immediate area. This “kicks” the local region into a single oscillation cycle, analogous to the reactive removal of CO in the spatially uniform system. In general, for “strong” oscillations or excitability, and “weak” diffusion, the pulse shape is determined by time-trace of concentrations in the homogeneous system. Different interior points in the pulse simply have different phases in the oscillation cycle, and the width of the pulse is proportional to its velocity [19]. In fact, pulse shapes in Fig.4 produced very well by mirror image of time-traces in Fig.2. Next we
Fig. 4 Concentration profiles for propagating reactive pulses. (a) and (c) profiled with $D_{CO}$ constant using the Imbihl and King prescriptions for the reconstruction dynamics respectively. Arrows indicate the part of the profile that determines the propagation velocity; (b) and (d) corresponding profiles using the percolative diffusion with $\theta_c = 0.6$. 
discuss the expected dependence of the propagation velocity, $V$, on the choice of $D_{CO}$. For models with constant $D_{CO}$, it follows trivially that $V$ is directly proportional to $\sqrt{D_{CO}}$ [18]. Thus, one expects a decrease in $V$ if one changes from constant $D_{CO}$ to percolative diffusion (3), and as one increases $\theta_c$, since then $D_{CO}$ decreases at any fixed $\theta_{ix1}$. See Fig.3. Below, we discuss in detail these issues separately for the two different prescription of reconstruction dynamics.

For prescription of Imbihl et al [5], a common feature of the reactive pulse, both when $D_{CO}$ is constant (Fig.4a), or given by (3) with $\theta_c=0.6$ (Fig.4b), is an extended interior region with insignificant coverage (and thus diffusion) of CO. Clearly, here, the above mentioned correspondence between pulse shape and time-trace would be precise. However, we find that the length of the pulse is actually shorter in Fig.4a where $V=0.126$ cm/s, than in Fig.4b with smaller $V=0.116$ cm/s. This just reflects the presence of significant CO-diffusion to the right at the tail end of the pulse in Fig.4a. This causes the pulse width to shrink relative to Fig.4b, where diffusion is inhibited at the tail end of the pulse (since $\theta_{ix1}$ is low there). It is also clear that here $V$ is determined primarily by behavior at the front of the pulse (indicated by an arrow in Fig.4a,b). Thus $V$ will be controlled by the value of $D_{CO}$ in that region, which is determined by the corresponding value of $\theta_{ix1}$ [for the case (3)]. Since $\theta_{ix1}$ is only slightly reduced from unity at the front of the pulse, $D_{CO}$ is not greatly reduced even for large $\theta_c$.

Indeed, Table I shows that the decrease in $V$, accounting for percolative diffusion using (3), is not significant.
Finally, we discuss behavior using the prescription of King and coworkers [12] for the reconstruction dynamics. Fig.4c,d show that the shape of the pulse is very different from the Imbihl model. But perhaps a more important observation is that in the "wake" of each pulse, the hex→1×1 transformation is slow, so $\theta_{1x1}$ only increases very slowly back towards unity (and $\theta_{CO}^{1x1}$ slowly decreases). Thus, the subsequent excited wave propagates into a medium with changing $\theta_{1x1}$ (and $\theta_{CO}^{1x1}$), so its velocity and shape is a function of time. Also, since $\theta_{1x1}$ is typically significantly below unity when the pulse is emitted, effects of percolative diffusion are expected to be greater. This is clear from Table I which shows that $V$ decreases significantly changing from constant $D_{CO}$ to percolative diffusion (3) and increasing $\theta_c$. For consistency here, we always measured $V$ at the point when the value of $\theta_{1x1}$ just in front of the pulse was about 0.85. (This is a point in time prior to that shown in Fig.4c,d.)

Table 1 Propagation velocity, $V$, versus percolation threshold, $\theta_c$, for $D_{CO}$ given by (3) with $D_{CO}^{1x1}=4\times10^{-4}$ cm²/s (except for the top row where $D_{CO}=4\times10^{-4}$ cm²/s is constant).

<table>
<thead>
<tr>
<th>$\theta_c$</th>
<th>$v$ cm/s (Imbihl)</th>
<th>$v$ cm/s (King)</th>
</tr>
</thead>
<tbody>
<tr>
<td>---</td>
<td>0.126</td>
<td>0.0341</td>
</tr>
<tr>
<td>0.0</td>
<td>0.123</td>
<td>0.0244</td>
</tr>
<tr>
<td>0.2</td>
<td>0.121</td>
<td>0.0263</td>
</tr>
<tr>
<td>0.4</td>
<td>0.120</td>
<td>0.0263</td>
</tr>
<tr>
<td>0.6</td>
<td>0.116</td>
<td>0.0188</td>
</tr>
<tr>
<td>0.8</td>
<td>0.106</td>
<td>0.0140</td>
</tr>
</tbody>
</table>
IV. SUMMARY

We have presented the first treatment of spatio-temporal behavior in CO-oxidation on Pt(100) accounting in a simple way for the percolative nature of CO-diffusion. This is done by selection of a suitable form for the dependence of the chemical diffusion coefficient, \( D_{CO} \), on the fraction, \( \theta_{1\times1} \), of the substrate in the 1x1-state on which true macroscopic diffusion is possible. As expected, we find that this results in a decrease in the propagation velocity of reactive O-rich pulses excited at defects at steps (compared to the traditional choice of \( D_{CO} \) as a constant with a value equal to that for a perfect 1x1-substrate). However the reduction in velocity is not great using the prescription of Imbihl et al [5] for the reconstruction dynamics. This is simply because \( \theta_{1\times1} \) is close to unity at the front of the pulse where the velocity is selected. The effect is greater for the prescription of King and coworkers [12].

REFERENCES


[14] The Ginzburg-Landau evolution equation for $\theta_{1x1}$ from Ref.[13] includes a Laplacian “diffusion” term, where the “diffusion” coefficient, $D_{1x1}$, is determined by the interface energy between adjacent patches of 1x1- and hex-substrate. Here we note that $D_{\text{CO}}$ always includes an analogous contribution due to the spatial coupling associated with reaction of species on distinct (adjacent) sites. See J.W. Evans and T.R. Ray, Phys. Rev. E **50**, 4302 (1994). However, this contribution to $D_{\text{CO}}$, as well as $D_{1x1}$, are very small, and do not play a significant role in spatial pattern formation.


CHAPTER 5. CHEMICAL DIFFUSIVITY AND WAVE PROPAGATION IN SURFACE REACTIONS: ANALYSIS OF BISTABLE AND UNSTABLE SYSTEMS


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ABSTRACT

Spatial pattern formation and wave propagation in surface reactions are controlled by the chemical diffusion of adsorbed reactant species. We emphasize that such diffusion invariably occurs in mixed adlayers, and is intrinsically non-linear due to the influence of coadsorbed species. These non-linearities are characterized, and shown to significantly influence spatiotemporal behavior in atomistic lattice-gas models of surface reactions. We consider two examples: trigger wave propagation in a bistable system characteristic of CO-oxidation; and removal of unstable NO+CO adlayers via dissociation-mediated NO-reduction.
Reaction-diffusion systems often exhibit a rich variety of complex spatiotemporal behavior. This behavior is understood to arise from the interplay between the non-linear reaction kinetics and the diffusion of reactant species. It can often be successfully described by mean-field (MF) reaction-diffusion equation analyses. Surface reactions on single crystal substrates under ultra-high vacuum conditions provide perfect two-dimensional (2D) examples of these systems. Here, MF analyses reproduce the observed mesoscopic characteristic lengths of spatial patterns, and the "rapid" wave propagation velocities, which derive from the high surface diffusivities of some adsorbed reactant species. However, such MF treatments ignore the influence on the reaction kinetics of spatial correlations and ordering, which are generally significant in two-dimensional adlayers. They also ignore non-linearities in diffusion, which we show are intrinsic to the mixed adlayers formed in these systems, as well as to ordered adlayers in general (cf. Ref.4).

Microscopic treatments using appropriate lattice-gas (LG) models could potentially incorporate the latter complicating features, thereby providing a more sophisticated treatment of non-equilibrium reactive adlayers, akin to that used to analyze equilibrium properties of non-reactive adlayers. Indeed, there have been many generic LG model studies examining influence of correlations and fluctuations in reactive 2D systems. The typical focus has been on deviations from MF reaction kinetics in spatially uniform systems, and on spatial
correlations, although some recent studies have considered wave propagation phenomena. However, these studies have focused on diffusion-limited reactions without input of reactants, and on 2D reaction models with instantaneous reaction or without high diffusivity of reactants. Thus, they do not apply to typical surface reactions where hop rates for some adspecies are usually many orders of magnitude greater than all other rates. Realistic LG modeling of such surface reactions must take into account that it is this high adspecies diffusivity which produces the observed strong hysteresis in the reaction kinetics and metastability in steady states.

Another consequence of high hop rates, relative to other rates, is the formation of mixed adlayers. However, despite this feature and the important role of diffusion in surface reactions, there has been little relevant analysis of chemical diffusion in mixed adlayers. In contrast, there have been extensive studies for single species adlayers. In both cases diffusion can be assessed by monitoring evolution of concentration profiles. These are often “artificially induced” in non-reactive systems, but they arise naturally as a result of pattern formation in reactive systems.

In this Letter, we first characterize non-linearities in the chemical diffusion in mixed adlayers of highly mobile species. These non-linearities invariably occur since the diffusion of each adspecies is influenced by the presence of coadsorbed species, even in the absence of interactions beyond site exclusion. Next, we show with two examples that these non-linearities can significantly influence the spatiotemporal behavior in typical surface reactions where diffusion rates for some adspecies dominate all other rates. The first example involves wave propagation and equistability in a bistable system characteristic of the CO+1/2O2→CO2
reaction. The second example involves the autocatalytic removal of unstable, mixed NO+CO adlayers via the NO+CO→CO₂+1/2N₂ reaction. In both cases, we compare behavior of atomistic LG models, in the relevant "hydrodynamic regime" of high adspecies diffusivity, with predictions from reaction-diffusion equations (with and without non-linear diffusion).

First we consider chemical diffusion in a mixed adlayer of two species, A and B, with (local) coverages \( \theta_A \) and \( \theta_B \), respectively. In general, a concentration gradient, \( \nabla \theta_K \), in one adspecies, \( K=A \) or \( B \), generates mass fluxes \( J_K \) in both adspecies A and B. Thus one writes

\[
\begin{pmatrix}
J_A \\
J_B
\end{pmatrix} = -D \begin{pmatrix}
\nabla \theta_A \\
\nabla \theta_B
\end{pmatrix}
\]

where

\[
D = \begin{pmatrix}
D_{AA} & D_{AB} \\
D_{BA} & D_{BB}
\end{pmatrix}
\]

is a tensor of chemical diffusion coefficients. Here we consider only the case where there are no interactions between adspecies for except site blocking, and restrict our attention to a square lattice of adsorption sites. Adspecies A and B can hop to any adjacent empty site at generally distinct rates, \( h_A \) and \( h_B \), respectively. The following features of \( D \) must apply: (a) \( D_{KK} \) reduces to \( D_K^0=\delta h_K \), for low coverages of both adspecies; in general \( D_{KK} \sim D_K^0 \) so we set \( D_{KK}=D_K^0 F_{KK} \); (b) \( F_{AB} \rightarrow 0 \), as \( \theta_A \rightarrow 0 \), and \( F_{BA} \rightarrow 0 \), as \( \theta_B \rightarrow 0 \), since the flux of species, \( K \), induced by a concentration gradient in the other species must vanish as \( \theta_K \rightarrow 0 \); (c) when \( \theta_A \rightarrow 0 \), \( F_{AA} \) corresponds to the generalized tracer diffusion coefficient, \( F_{tr}(\theta_B) \) for a single particle A diffusing through a surrounding "bath" of particles B with different hop rate;
similar results apply for \( F_{BB} \) when \( \theta_B \rightarrow 0 \); (d) since \( J_K \) must vanish in a “jammed” system, where \( \theta_A + \theta_B = 1 \) and \( \nabla \theta_A = -\nabla \theta_B \), one must have \( F_{KA} = F_{KB} \) when \( \theta_A + \theta_B = 1 \). Below, we focus on the diffusion of species A, and naturally consider three regimes: (i) \( h_A << h_B \); (ii) \( h_A >> h_B \); (iii) \( h_A \) comparable to \( h_B \).

In Regime (i), A diffuses in a background of “highly dynamic” coadsorbed B. The limit \( \theta_A \rightarrow 0 \), which corresponds to tracer diffusion of a “slow particle” in a bath of much more mobile particles, has been considered previously. Here, it was argued that the lack of correlations in the B adlayer implies mean-field behavior, \( F_{AA} = F_{tr}(\theta_B) = 1 - \theta_B \), where the decrease from unity reflects the fraction of blocked sites. Extending this result by analysis of the relevant master equations, neglecting all correlations, indicates that in fact \( F_{AA} = 1 - \theta_B \), and \( F_{AB} = \theta_A \) for arbitrary coverages of A and B. Finally, in the context of surface reactions, we note that the highly mobile adspecies B would control spatiotemporal behavior, so in this respect diffusion of A would not be important.

In Regime (ii), A diffuses through an effectively static disordered environment created by the coadsorbed species B. Since there are no interactions between adspecies, it is possible to show that the master equations for diffusion of species A reduce to single-particle equations species. Thus, the chemical diffusion coefficient, \( D_{AA} \), is identical to the single-particle diffusion coefficient. Furthermore, the theory of (single-particle) transport in percolative systems applies to show that \( F_{AA} = F_{perc}(\theta_B) \) decreases with increasing \( \theta_B \) from unity, when \( \theta_B = 0 \), to zero at the percolation threshold, \( \theta_B = \theta^* \), where paths of sites not occupied by B cease to connect opposite sides of the system. Behavior near the threshold is
described by universal exponents, but the values of $\theta^*$ and of $D_{AA}$ depend on the details of
the correlations in the B adlayer. Except for $\theta_B$ close to $\theta^*$, one can show that $^{17,18}$
$$F_{\text{perc}} = 1 - (\pi - 1)\theta_B - \alpha \theta_B^2,$$
where correlations effect $\alpha$. $^{18}$

Our remarks above imply that a gradient in the coverage of the disordered "static"
background of coadsorbed B also induces a diffusive flux of species A (although this feature
has not been recognized in modeling of surface reactions). Since the master equations for
diffusion of A reduce to single-particle equations, even for a non-uniform background of B,
the magnitude of this flux must be proportional to $\theta_A$. Thus one can write $F_{AB} = \theta_A G(\theta_B)$.
Then since from above $F_{AA} = F_{AB}$ at "jamming", it follows that $G(\theta_B) = F_{\text{perc}}(\theta_B)/(1-\theta_B)$.

In Regime (iii), where the mobility of A and B are "comparable", analysis is more
difficult. We first make some general observations regarding the anticipated behavior of $F_{AA}$
which we naturally regard as a function of $\theta_B$ (parameterized by $\theta_A$). Comparing Regimes (i)
and (ii) shows that a static background of B impedes the diffusion of A more severely than a
highly dynamic background (with the same $\theta_B$). Thus, one expects a progressive decrease in
$F_{AA}$ with decreasing $h_B/h_A$. General support for this idea comes from studies of "dynamic
percolation" where A diffuses in a dynamically disordered lattice on which the state of sites
or bonds fluctuates between allowing and blocking transport: here the diffusivity of A is
progressively inhibited as the fluctuation frequency (corresponding to $h_B$) decreases relative
to the hop rate for species A. $^{16}$ Explicit results for $F_{AA}$, in the $\theta_A \to 0$ limit, come from a
previous analysis of generalized tracer diffusion, $^{14}$ and confirm this postulated behavior.
Fig.1 summarizes schematically the behavior of $F_{AA}$ for different $h_B/h_A$. Note that $F_{AA}$
Fig. 1 Decrease of the diffusion tensor component, $D_{AA} = D_A^0 F_{AA}$, with increasing $\theta_B$. The functional form only is independent of $\theta_A$ for $h_A \ll h_B$ and $h_A \gg h_B$. Curves shown for $h_A = h_B$ correspond to $\theta_A = 3/4, 1/2, 1/4, 0^+$. and terminate at values of $\theta_B = 1 - \theta_A$. 
reduces to single curve in both the limiting regimes, but otherwise is represented by a family of curves (for varying $\theta_B$).

A complete analysis of $D$ is readily achieved in the case $h_A=h_B(=h$, say), where one can exploit special physical and symmetry properties. Here the total coverage must satisfy the classic diffusion equation for a non-interacting single-species lattice-gas\textsuperscript{15} with hop rate $h$, so it follows that $F_{AA}+F_{BA}=F_{AB}+F_{BB}=1$. Furthermore, if $F_{AA}=F_{BA} (\theta_B)$, then by symmetry $F_{BB}=F_{BA} (\theta_A)$, so $D$ is determined by the single function $F_{g}(\theta)$ (and by $D^0$). Thus, we now characterize $F_{g}(\theta)$. In the limit $\theta' \to 0$, $F_{0g}(\theta)=F_{g}(\theta)'=(1-\theta)f(\theta)$ reduces to the conventional tracer diffusion coefficient for a particle in a bath of particles with the same hop rate,\textsuperscript{19} where the “correlation factor” satisfies $f(\theta)=1-0.62\theta+0.08\theta^2$. At jamming, where $\theta' \to 1-\theta$, one has $F_{AA}=F_{AB}=1-F_{BB}$, so $F_{1g}(\theta)+F_{g}(1-\theta)=1$, indicating that $F_{1g}(\theta)=1-\theta$. It just remains to interpolate between these limits, which can be done exactly in this special case.\textsuperscript{20} See also Fig. 1.

Next, we compare behavior of two LG reaction models in the hydrodynamic regime with the predictions of reaction-diffusion equations incorporating three treatments of diffusion: (S) the standard linear choice $D_{KK}=D_{K}^0\delta_{K,K'}$; (M) a modified choice $D_{KK}=D_{K}^0[(1-\theta_k)\delta_{K,K'}+\theta_k(1-\delta_{K,K'})]$, treating all coadsorbed species as highly dynamic [cf. Regime (i)], thus generally underestimating their influence; and (E) an exact treatment (apart from approximations to $F_{perc}$ or $F_{tr}$) as outlined above.

**BISTABLE SYSTEMS.** Here we consider systems with continual adsorption of reactants and conversion to products. A typical scenario is that a “poisoned state” with low
reactivity (due to a high coverage of some reactant) coexists with a "reactive steady state" with high reactivity (and low coverage). At least this scenario applies for some finite range of relative adsorption rates, characterized as the "bistable region". In a spatially inhomogeneous system, where the poisoned state is separated from the reactive state by a planar interface, the more stable of the two states displaces the other, thereby creating a chemical wave. Scanning the bistable region, the relative stability of the states switches, and thus the velocity of the chemical wave changes sign at a unique equistability point. Clearly there will be a large mass flux of reactants at the interface due to the large coverage gradients. Thus the detailed nature of the chemical diffusion will affect the structure of the interface, the propagation velocity, and the location of the equistability point.

We analyze such behavior in an A+B$_2$ lattice-gas (LG) reaction model with the steps

\[ A(\text{gas}) + * \rightarrow A(\text{ads}), \quad B_2(\text{gas}) + 2* \rightarrow 2B(\text{ads}), \quad \text{and} \quad A(\text{ads}) + B(\text{ads}) \rightarrow AB(\text{gas}) + 2*, \]

where "gas" denotes gas phase, "ads" denotes adsorbed species, and * denotes an empty surface adsorption site. Thus A(gas) adsorbs at rate $P_A$ on single empty sites, B$_2$(gas) adsorbs at rate $P_B$ on adjacent pairs of empty sites, and adjacent A(ads) and B(ads) react at rate $k_{\text{react}}$ to form the product AB(gas) [for each A(ads)-B(ads) pair]. We also allow hopping of A(ads) and B(ads) to adjacent empty sites with rates $h_A$ and $h_B$, respectively. Below, we set $P_A + P_B = 1$, and $k_{\text{react}} = 1$. The model mimics CO-oxidation where A$\leftrightarrow$CO and B$_2$$\leftrightarrow$O$_2$. For finite hop rates, the model exhibits a discontinuous transition from a reactive state with low
to an A-poisoned state with $\theta_A = 1$, as $P_A$ increases above some value $P^*$. The reactive (poisoned) state is only metastable above (below) $P^*$. Thus, e.g., for $P_A < P^*$, the reactive state displaces the metastable poisoned state creating a trigger or chemical wave of velocity $V_t$, which vanishes as $P_A \to P^*$. In the "hydrodynamic regime" where just $h_A$, or both $h_A$ and $h_B$, become much larger than the other rates, fluctuations are quenched and the lifetimes of the metastable states diverge, so bistability is achieved, and $P^*$ becomes the equistability point. Since CO(ads) is highly mobile, and O(ads) is relatively immobile, we focus on the case $h_A \gg 1$ and $h_B = 0$. Simulation curves for the velocity $V_t$ versus $P_A$ shown in Fig. 2a display an interesting "crossing feature" (cf. Ref. 10). One can write $V_t = 2.2(C + h_A)^{1/2}(0.397 - P_A) + 0.08$, for $P_A = 0.397$ and $C = O(1)$ (cf. Ref. 9). This implies that $P^* = 0.397 \pm 0.001$ in the hydrodynamic limit ($h_A \to \infty$), and that the deviations of the scaled velocity, $u_t = V_t/h_A^{1/2}$, from its limiting form scale like $h_A^{-1/2}$. Next we compare this simulation result for $P^*$ with predictions from MF reaction-diffusion equations. Incorporating the standard (S) treatment of diffusion yields $P^* = 0.442$; the modified (M) treatment yields $P^* = 0.425$; an "exact" (E) treatment, using $F_{perc} = 1 - (\pi - 1)\alpha - \alpha^2$ with $\alpha = 0.775$ to match an assumed random percolation threshold of $\theta^* = 0.407$, yields $P^* = 0.406$. (E) does not precisely recover the exact value of $P^*$ since it ignores correlations in the immobile B-adlayer which affect the reaction kinetics, steady states, percolation, and diffusion properties.

One can account for these spatial correlations utilizing a recently developed a "hybrid" simulation procedure, or analytic dynamic-cluster approximations for the reaction
Fig. 2 Propagation of a planar trigger wave in the A+B₂ model with mobile A (hop rate of h), which mimics CO-oxidation: (a) propagation velocity, $V_t$ (in lattice spacings/unit time), versus $P_A$, for various h (shown); (b) scaled propagation velocity, $u_t$, versus $P_A$, with h=512, from simulations and predictions from correlated reaction-diffusion equations\(^1\) with various prescriptions of diffusion.
In particular, such an analysis shows that the percolation threshold is shifted up to \( \theta^* = 0.435 \), indicative of weak clustering. From analysis of reaction-diffusion equations accounting for these correlations, one obtains estimates of \( P^* = 0.440 \) (S), 0.419 (M), and 0.398 (E). For the treatment (E), we use the quadratic form for \( F_{\text{perc}} \) adjusting \( \alpha \) to match the shifted \( \theta^* \). More details will be presented elsewhere.\(^8\) Results for \( v_t \) versus \( P_A \) are shown in Fig.2b. The treatment (S), which ignores the influence of coadsorbed species on diffusion, substantially overestimates \( v_t \). The treatment (M), which accounts for but underestimates this influence, does somewhat better. Our “exact” treatment (E) almost perfectly matches the simulation results. These results demonstrate the significant influence of chemical diffusion on wave propagation [and the precision of (E)].

To test the influence of non-linearities in chemical diffusion for Regime (iii), it is also natural to consider the \( A+B_2 \) model for the case \( h_A=h_B=h>1 \). Simulation curves for \( V_t \) versus \( P_A \) reveal similar crossing behavior as in Fig.2a, and imply \( P^* = 0.430 \pm 0.002 \). MF reaction-diffusion equations yield estimates of \( P^* = 0.456 \) (S), 0.444 (M), and 0.430 (E) for various treatments of diffusion. Again this demonstrates the importance of non-linearities in chemical diffusion in determining equistability. Note that for this case, spatial correlations in the adlayer vanish for large \( h \) since both adspecies are mobile, so the MF treatment of reaction kinetics becomes valid.

**UNSTABLE SYSTEMS.** Here we consider a system involving the same reaction step as for the above bistable system (again with rate \( k_{\text{react}} \). But now we suppose \( B(\text{ads}) \) is
supplied by the dissociation of an adsorbed reactant, BC(ads), and that dissociation requires an adjacent empty adsorption site (and occurs at rate \( k_{\text{diss}} \)). Thus one has

\[
\text{BC(ads)} + \cdot \rightarrow \text{B(ads)} + \text{C(ads)}, \quad \text{and} \quad \text{A(ads)} + \text{B(ads)} \rightarrow 2\text{AB(gas)} + 2\cdot
\]

If there is no adsorption or desorption of reactant species, then clearly a surface completely covered by a mixed adlayer of A(ads) and BC(ads) constitutes a steady state. However it is unstable in that creation of empty sites or regions in this adlayer can lead to dissociation and subsequent reaction, which in turn creates more empty sites, and thus leads to further dissociation, reaction, and autocatalytic removal of the adlayer. This scenario applies for NO-reduction by CO on Pt(100), where "surface explosions" have been observed upon heating a NO+CO covered surface to around 370K, thereby activating limited desorption of reactants.\(^{22}\)

Thus, we analyze a simplistic LG model for the NO+CO reaction based on the above steps where \( \text{CO} \leftrightarrow \text{A} \), \( \text{O} \leftrightarrow \text{B} \), and \( \text{N} \leftrightarrow \text{C} \). Since N is removed from the surface by recombinative desorption, we also include the step \( \text{C(ads)} + \text{C(ads)} \rightarrow \text{C}_2\text{(gas)} + 2\cdot \) at rate \( k_{\text{des}} \). We use the experimental values\(^{22}\) for rates on Pt(100) at 400K of \( k_{\text{react}}=1.1 \text{s}^{-1} \), \( k_{\text{diss}}=0.13 \text{s}^{-1} \), and \( k_{\text{des}}=0.03 \text{s}^{-1} \). In addition, we let CO(ads), NO(ads), and N(ads), hop to adjacent empty sites at rate \( \gg 1 \text{s}^{-1} \); O(ads) is assumed immobile. Presumably the diffusion of CO(ads) and NO(ads) is similar. Assigning the same hop rate for N(ads) is done to simplify our analysis, but should not affect qualitative behavior. A square lattice of
adsorption sites is used since reconstruction of the 1x1-Pt(100) surface is not significant for the processes of interest.22

We have performed simulations with this model of the removal of randomly mixed NO+CO adlayers. Starting with an empty region in the otherwise covered surface, after a transient period, an expanding reaction front develops corresponding to "a wave of transition out of an unstable state". It becomes asymptotically planar with constant propagation velocity, $V_u$. Here we determine $V_u$ (in lattice spacings/sec) and its dependence on the composition of the NO+CO covered portion of the surface. To this end, it suffices to consider the propagation of a planar front ahead of which is the unstable NO+CO covered surface, and in the wake of which is any excess reactant [i.e., O(ads) if $\theta_{NO}>\theta_{CO}$, and CO(ads) if $\theta_{NO}<\theta_{CO}$]. In Fig.3, we show "exact" simulation results for the scaled velocity $u_u=V_u/h^{1/2}$, for a range of $\theta_{NO}$, as well as predictions from various MF reaction-diffusion equation analyses. Such an analysis for the standard description of diffusion (with $D_{CO}=D_{NO}=D_N=a^2h$) predicts a velocity substantially higher than the exact result. This is expected since the interference of coadsorbed species on diffusion is ignored. We also examine refined treatments of diffusion, analogous to (M) and (E) above, although complicated by the presence of multiple adsorbed species. Results for such treatments are similar, and match simulation results. Again this demonstrates the significant influence of non-linearities in chemical diffusion on wave propagation. Finally, we note that in modified models for this reaction, results from (M) and (E) differ somewhat, the latter being more precise.

SUMMARY. A precise description of spatiotemporal behavior in surface reactions models is provided by utilizing an appropriate treatment of chemical diffusion in mixed
Fig. 3 Scaled propagation velocity, $v_u$, of a planar wave of transition from an unstable NO+CO covered surface, versus the fraction, $\theta_{NO}$, of the covered surface occupied by NO. Comparison of simulations and predictions of reaction-diffusion equations with various prescriptions of diffusion. Scaled velocity in the simulation was determined by extrapolating results for $h \leq 200$. See text for units.
adlayers. Nonlinearities in the diffusion are shown to significantly affect chemical wave propagation in both bistable and unstable systems. Incorporation of adspecies interactions would produce even more dramatic deviations from traditional picture of constant diffusion coefficients.

ACKNOWLEDGEMENTS

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12. With instantaneous reaction, reacting adspecies cannot occupy the same local region of space in the limit of high diffusivity. Thus mixed adlayers do not occur for two-species models, and chemical diffusion coefficients are constants in the absence of adspecies interactions.


20. J. Quastel, Comm. Pure Appl. Math. XLV, 623 (1992). Results therein can be used to show that $F_r(\theta) = \frac{\theta' + \theta F_r(\theta' + \theta)}{\theta' + \theta}$, for $h_A = h_B \to \infty$.


CHAPTER 6. CHEMICAL DIFFUSIVITY AND WAVE PROPAGATION IN
A LATTICE-GAS MODEL MIMICKING CO-OXIDATION ON SURFACES
WITH HIGH CO-MOBILITY

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ABSTRACT

We analyze spatiotemporal behavior in a lattice-gas model for the monomer-dimer reaction
on surfaces, which mimics catalytic CO-oxidation. The model includes a mobile monomer adspecies (representing CO), an immobile dissociatively adsorbed dimer species (representing O), and a finite reaction rate (for CO₂ production). We characterize in detail the propagation of the chemical wave produced when the stable reactive steady-state of the model displaces the metastable CO-poisoned state. In the regime of high CO-mobility, propagation can be described directly within a “hydrodynamic” reaction-diffusion equation formalism. However, we show that the chemical diffusivity of CO is non-linear, reflecting the percolative nature of CO-transport through a background of immobile O. We also emphasize that gradients in the coverage of immobile O induce
a diffusive flux in the highly mobile CO. These features significantly influence wave propagation and structure. Our analysis accounts for the feature that in this hydrodynamic regime, correlations persist in the distribution of adsorbed immobile O, which influence the reaction kinetics, the steady states, and the percolation and diffusion properties. To this end, we utilize a “hybrid” approach which incorporates a mean-field reaction-diffusion treatment of adsorbed CO, coupled with a lattice-gas treatment of adsorbed O.

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I. INTRODUCTION

Surface reactions on single-crystal substrates, under ultra-high vacuum conditions, exhibit a rich variety of spatiotemporal behavior [1]. Traditionally, such behavior is described by mean-field (MF) reaction-diffusion equations with Fickian diffusion and constant chemical diffusion coefficients, D [1]. This approach ignores correlations or ordering, and corresponding fluctuations, in the adlayer which result from interactions between adspecies, from limited mobility of adspecies, or from the reaction process itself. These effects clearly influence the non-linear reaction kinetics and the steady-state coverages [2]. However, they also influence the chemical diffusion of adspecies, which controls the chemical wave propagation and spatial pattern formation in these systems. Furthermore, here we also emphasize that the traditional MF treatments ignore the feature that chemical diffusion typically occurs in mixed adlayers, where diffusion is intrinsically non-linear due to the influence of coadsorbed adspecies.
These complicating features of adlayer ordering and fluctuations, and of mixed adlayers, can in fact be treated within atomistic lattice-gas (LG) models. [2-6] Indeed, LG models have been applied to study a range of two-dimensional (2D) reaction systems, however most studies have not realistically treated surface reactions. Apart from simplifying assumptions regarding the reaction mechanism, the adspecies interactions, and the rates for various processes (adsorption, desorption, reaction), the crucial role of the high mobility of some adspecies has generally not been appreciated or incorporated into the models. Indeed, hop rates for the most mobile adspecies are often many orders of magnitude larger than all other rates (including that for reaction). [7] This feature clearly results in the mixed adlayers mentioned above, and also determines the mesoscopic length scale, \( L \sim (D/k_c)^{1/2} \), of the spatial patterns, and the “large” wave propagation velocities, \( V \sim (k_c D)^{1/2} \), observed in these systems. [1] Here \( k_c \) is an effective rate for the overall reaction process. However, there are also more subtle effects. High mobility quenches fluctuations that produce transitions between distinct steady states “branches”, should they exist. [6,8] This results in the strong metastability and hysteresis often observed in experiments, and characteristic of mean-field treatments.

Our focus here is on chemical diffusion and spatiotemporal behavior in a simplistic LG reaction model for CO-oxidation, with highly mobile adsorbed CO, and immobile adsorbed O. The model supports a state of high reactivity with low CO coverage, for lower CO partial pressures (\( P_{CO} \)), and a completely poisoned CO-covered state. As \( P_{CO} \) increases above a critical value, \( P^* \), the reactive state changes from stable to metastable, and the opposite occurs for the poisoned state. Fluctuations then induce a discontinuous transition from the reactive state to the poisoned state. One can also consider the evolution of an
interface between the reactive state and the poisoned state. When $P_{\text{CO}} < P^*$, for example, the stable reactive state displaces the metastable poisoned state leading to chemical wave propagation. As indicated above, high CO mobility quenches fluctuations, increasing the lifetime of the metastable states, and thus producing mean-field type bistability and deterministic wave propagation. However, despite the realization of mean-field type behavior in this regime, chemical diffusion is not necessarily described by constant $D$. The only property of $D$ that is guaranteed is that it will scale like the hop rate for adsorbed CO. In this work, we provide a complete characterization of the non-trivial nature of chemical diffusivity, and its consequences for wave propagation.

First, in Sec.II, we describe in detail the LG monomer-dimer reaction model mimicking CO-oxidation on surfaces. We also present simulation results for this model, focusing on the propagation of chemical waves. Then, in Sec.III, we provide some general remarks concerning chemical diffusion. We describe effective diffusivity for finite CO-mobility, and an explicit prescription for diffusion coefficients in the "hydrodynamic" regime of high CO-mobility, accounting for the percolative nature of CO-diffusion through the disordered environment of coadsorbed immobile O. A direct analysis of spatiotemporal behavior in the hydrodynamic regime is presented in Sec.IV, and results are compared with those in Sec.II. This analysis is achieved by implementing a recently developed "hybrid" treatment which combines MF reaction-diffusion equations to describe the highly mobile CO(ads), coupled with a LG treatment of coadsorbed immobile O. A discussion of the limitations of the model, and of refinements needed to facilitate comparison with experiment, is given in Sec.V. Some final remarks are provided in Sec.VI.
II. LATTICE-GAS MODEL MIMICING CO-OXIDATION ON SURFACES

A. Description Of The Monomer-Dimer Reaction Model

The lattice-gas (LG) monomer-dimer surface reaction model mimicking CO-oxidation includes the following simple steps: CO(gas) adsorbs on single empty sites at rate \( p_{\text{CO}} \); \( \text{O}_2\)(gas) adsorbs dissociatively on adjacent empty sites at rate \( p_{\text{O}_2} \); adjacent \( \text{CO}(\text{ads}) \) and \( \text{O}(\text{ads}) \) react to form the product \( \text{CO}_2\)(gas) at rate \( k \), leaving two empty surface sites. In addition, \( \text{CO}(\text{ads}) \) can hop to each adjacent empty site at rate \( h \). These steps are summarized schematically as:

\[
\begin{align*}
\text{CO}(\text{gas}) + E & \rightarrow \text{CO}(\text{ads}), & \text{O}_2(\text{gas}) + 2E & \rightarrow 2\text{O}(\text{ads}), \\
k & & h \\
\text{CO}(\text{ads}) + \text{O}(\text{ads}) & \rightarrow \text{CO}_2(\text{gas}) + 2E, & \text{CO}(\text{ads}) + E & \rightarrow E + \text{CO}(\text{ads})
\end{align*}
\]

Here 'gas' denotes gas phase species, 'ads' adsorbed species, \( E \) an empty surface site, and \( 2E \) an adjacent empty pair. The impingement rates, \( p_{\text{CO}} \) and \( p_{\text{O}_2} \), for CO(gas) and \( \text{O}_2\)(gas), respectively, are simply related to the partial pressures for these species; \( k \) denotes the reaction rate for each adjacent pair of \( \text{CO}(\text{ads}) \) and \( \text{O}(\text{ads}) \). Henceforth, we normalize the impingement rates such that \( p_{\text{CO}} + p_{\text{O}_2} = 1 \), and we set \( k = 1 \). Adspecies interactions, other than reaction of adjacent \( \text{CO}(\text{ad}) \) and \( \text{O}(\text{ad}) \), are ignored. The model is implemented on a square lattice of adsorption sites.
Some previous discussion of this model can be found in Ref.s [4,5] for h=0, and Ref.s [8,9] for h>0. We are primarily interested in the regime where h>>1, corresponding to the typical experimental situation where the CO(ads) hop rate, h, is many orders of magnitude larger than the other rates. With this in mind, it is appropriate to emphasize that we have chosen k finite here, rather than infinite (instantaneous reaction), as in several other studies. [3,6,10] Choosing infinite k does not qualitatively change the steady-state behavior or kinetics for spatially uniform systems. However, in the h→∞ limit for models with infinite k, only one reactant can have non-zero local coverage at a macroscopic point, [11] and this produces an artificial situation with regard to chemical diffusion and wave propagation. See Appendix A.

B. The Discontinuous Poisoning Transition

The key feature of this model of interest here is the occurrence of a discontinuous phase transition from a stable reactive steady-state to a stable CO-poisoned “absorbing” state, with increasing p_{CO}. The location of the transition is denoted by p_{CO}=p^*, where p^*=p^*(h) depends on h. A metastable extension of the reactive state also exists for p^*<p_{CO}<p_{s+}, where p_{s+}=p_{s+}(h) denotes an “upper spinodal”. Correspondingly, a metastable CO-poisoned state exists for some range p_{s-}<p_{CO}<p^*, where p_{s-}=p_{s-}(h) denotes a “lower spinodal”. Clearly, because of its “absorbing” nature, the CO-poisoned state exists as a steady-state for all p_{CO}. It is stable for p>p_{CO}, metastable for p_{s-}<p_{CO}<p^*, and unstable p_{CO}<p^*.

As could be anticipated from the general discussion in Sec.I of the effect of diffusion on metastability, increasing h in this monomer-dimer reaction model leads to an increase in the lifetime of the metastable states, and also broadens their existence range. [6,8,9,11] For example, in our model with k=1, the width of the existence region for the metastable reactive
state increases dramatically from 0.005, when \( h=0 \), to 0.103, when \( h \to \infty \). More specifically, one finds that \( p^*(0)=0.432 \) and \( p_s(0)=0.437 \), whereas \( p^*(\infty)=0.397 \) (see below) and \( p_s(\infty)=0.500 \). One ramification is that determination of the location of the poisoning transition by monitoring the kinetics for various \( P_{CO} \) (and noting the onset of poisoning) tends to overestimate \( p^* \), since the system gets trapped in the metastable reactive state for \( P_{CO} \) slightly above \( p^* \). Such corrupted estimates can be avoided either by performing an appropriate "epidemic analysis", or by implementing the "Constant-Coverage Ensemble" method. Estimates from the latter approach for \( p^* \) versus \( h \) are reported in Table I.

Table 1. Dependence of the discontinuous poisoning transition, \( p^*(h) \), on the CO hop rate, \( h \), for the LG monomer-dimer surface reaction model with \( k=1 \).

<table>
<thead>
<tr>
<th>( h )</th>
<th>( p^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.4328</td>
</tr>
<tr>
<td>1</td>
<td>0.4227</td>
</tr>
<tr>
<td>4</td>
<td>0.4152</td>
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<tr>
<td>16</td>
<td>0.4070</td>
</tr>
<tr>
<td>32</td>
<td>0.4044</td>
</tr>
<tr>
<td>64</td>
<td>0.4027</td>
</tr>
</tbody>
</table>

C. Propagation Velocity Of The Chemical Wave

The chemical waves analyzed here are produced, for \( P_{CO} \leq p^*(h) \), when the stable reactive steady-state displaces the metastable or unstable CO-poisoned state, which is separated from it by an on-average planar interface. See Fig.1. This phenomena was noted in
the original paper of Ziff et al [3] on the monomer-dimer model with infinite \( k \) and \( h=0 \) (the so called ZGB model). It has been studied in detail more recently for extensions of the ZGB model including adspecies diffusion. [6,10] One expects that for our model with \( k=1 \) and any (fixed) \( h \), the propagation velocity, \( V \), vanishes linearly with
\[
\Delta = \rho^*-p_{CO} \geq 0, \text{ as } \Delta \to 0, \text{ due to a disappearance of the driving force for the reactive state to displace the CO-poisoned state on approaching the transition.} [14]
\]
Next, we elucidate the dependence of \( V \) on \( h \) (for fixed \( \Delta \)). One can argue that \( V \) should scale like \( \frac{\ell}{\tau_c} \), where
\[
\tau_c=1/k_c=O(1)
\]
is a characteristic time for the reaction process, and \( \ell_c \) is an overall characteristic length. This length is determined by both the diffusion length, \( \ell_d=\tau_ch^{1/2} \), and a "direct spatial coupling" length, \( \ell=O(1) \), due to reaction between distinct adspecies at neighboring sites. (Here, all distances are measured in units of the lattice constant.) Consideration of generalized Spatial Contact Models [15] for spreading or propagation due to both direct spatial coupling or contact, as well as due to conventional diffusion, suggests that \( \ell_c^2 \approx \ell_d^2 + \ell^2 \).

\[
V=\rho(\rho+h)^{1/2}\Delta.
\]  

By comparison with conventional mean-field reaction-diffusion equation analyses, where \( V \sim (k_\ell D)^{1/2}\Delta \), one might define an effective diffusion coefficient, \( D_{eff} \), in context of chemical waves, which scales like \( D_{eff} \sim A^2(\rho+h) \). See also Ref.[10] and Sec.III.
Fig. 1 Simulated configurations for cuts through the interface between the reactive steady-state (on the top) and the CO-poisoned state (on the bottom) at the discontinuous transition, $p_{\text{CO}} = p^*(h)$, for: (a) $h=0$; (b) $h=16$; (c) $h=512$. Mobile CO is represented by '•', and immobile O by 'o'.
The behavior described above was indeed observed using conventional simulations to
determine $V$ as a function of $p_{CO} \leq p^*(h)$, for various choices of $h \geq 0$. The results are shown in
Fig.2. Here $V$ is determined from the variation of the location of the interface defined as in
Ref.[8]. Of course, various definitions of this location are possible, but all give the same $V$
for steady-state propagation. First, we note that the impingement rates corresponding to $V=0$
coincide exactly with the $p^*$ determined independently above from the Constant-Coverage
Ensemble method. However, the most dramatic feature apparent in Fig.2 is the "near-
crossing" of curves for different $h$, which occurs at $p_{CO} = p_x = 0.397$ and $V = V_x = 0.08$. This
type of behavior is certainly consistent with eq.(1), which shows that the slope of such curves
must diverge, as $h \to \infty$. Perhaps, most importantly, one can conclude from eq.(1) that the
"crossing point" yields an estimate of

$$p^*(h \to \infty) = p_x = 0.397, \text{ when } k=1. \quad (2)$$

In this way, simulations for a range of "small" $h$ can be reliably extrapolated to assess
limiting behavior of $p^*$ in the physically relevant regime of very large $h$.

It is also appropriate to extract from this simulation data estimates for the values for the
parameters, $A$ and $B$, in eq.(1). This is most naturally achieved by examining the quasi-linear
variation of $(dV/d\Delta)^2 = D_{eff} = A^2(B+h)$ with $h$ (for large $h$). From this behavior using values
for $dV/d\Delta$ at the crossing-point for large $h$, we find that $A=2.2\pm0.3$ and a $B$-value of order
unity. Finally, it is appropriate to note that analogous "near-crossing" behavior of $V$ versus
$p_{CO}$ curves, for various $h$, was observed previously by Goodman et al. [10] for the monomer-
Fig. 2 Chemical wave propagation velocity, $V$, versus $p_{CO}$ (below $p^*$), for various $h$ (shown). The dashed vertical line shows limiting behavior for $h \to \infty$. 
Dimer reaction model with infinite \( k \) (instead of \( k=1 \)), but retaining mobile CO with hop rate \( h \), and immobile O. See Appendix A.

D. Structure Of The Chemical Wavefront

We now discuss in more detail the structure of the chemical wave front. From Fig. 1, it is apparent that there are fluctuations in the location of the interface between the reactive and CO-poisoned states, and that these are particularly dramatic for small \( h \). The total amplitude of these fluctuations, \( \xi \), is naturally decomposed into contributions due to intrinsic fluctuations, \( \xi_i \), and contributions due to long-wavelength fluctuations, \( \xi_0 \), where \( \xi^2 = \xi_i^2 + \xi_0^2 \). [6,16] For \( h=0 \), large intrinsic fluctuations occur when \( p_{CO}=p^* \) (and these are the dominant feature in Fig. 1a), although they are significantly reduced when \( p_{CO}<p^* \). Fig. 1 also indicates that increasing \( h \) above zero, when \( p_{CO}=p^* \), quenches the intrinsic fluctuations initially [6] (or at least they do not grow significantly, depending on the precise definition of the interface location, and of \( \xi_i \)). However, they are expected to increase slowly with larger \( h \). For example, “diffusion front” studies suggest that \( \xi_i \sim h^{2/7} \), defining the interface as the “shore-line” of the CO-covered region. See Appendix B.

It has also been shown [6,10] that the long-wavelength fluctuations are described by the stochastic KPZ-equation, [17] for \( p_{CO}<p^* \). As a result, the amplitude of these fluctuations, measured over a locally-equilibrated section of the interface of length \( L \), must scale like \( \xi_0 \sim 24^{-1/2}(\gamma L \nu)^{1/2} \), where \( \gamma \) measures the amplitude of the shot-noise in the KPZ equation, and \( \nu \) denotes the kinetic surface tension at the interface. [10,17] Comparison of KPZ and mean-field reaction-diffusion equation analyses of the evolution of curved
interfaces indicates that $v \sim h$, for large $h$. [6] This increase in the kinetic surface tension with $h$ quenches the long-wavelength fluctuations. Thus, for example, one has $\xi_0 \sim \gamma^{1/2} h^{-1/4}$, on the characteristic length scale, $L \sim \xi_0 \sim h^{1/2}$, for large $h$. Finally, we note that while the long-wavelength fluctuations are not of the KPZ type precisely at the transition, [6,10] it is clear that they are still quenched with increasing $h$.

The key observation from the above analysis is that all fluctuations "quickly" become insignificant relative to the characteristic length scale, $\xi_0 \sim h^{1/2}$, with increasing $h$. This is entirely consistent with the general statements in Sec.I concerning the enhancement of metastability and the attainment of "mean-field behavior", with increasing surface mobility. See Ref.s [6,8,10,11].

Finally, in Fig.3, we show concentration profiles for cuts through the "equilibrated" reaction front at $p_{CO}=p^*$, obtained from simulations of systems with a fixed width of 600 lattice spacings. Here, $\theta_{CO}$ and $\theta_O$ denote the mean coverage of CO and of O, respectively, along rows of sites orthogonal to the direction of propagation. From these profiles, one can clearly see the increase with $h$ of the "characteristic width" of the front (which corresponds to $\xi_0$). The smooth nature of the profile and the primary contribution to the width for $h=0$, in Fig.3a, is due to the intrinsic fluctuations. For large $h$ (Fig.3c), the profile appears to be developing a non-analytic nature, quite distinct from that anticipated from a description of chemical waves using conventional reaction-diffusion equations with constant diffusion coefficients. [18] Indeed, we shall show in Sec.IV that this unusual structure is associated with the percolative nature of CO-diffusion in this system.
Fig. 3 Simulated coverage profiles across the interface between the reactive steady-state (on the left) and the CO-poisoned state (on the right) at the discontinuous transition, $p_{CO}=p^*(h)$, for: (a) $h=0$; (b) $h=16$; (c) $h=512$. The position ‘x’ is given in units of lattice constants. The length, $\Delta x$, of profile shown is chosen as the same fixed multiple of $\xi \propto A(B+h)^{1/2}$, for each $h$-value [specifically, $\Delta x = 7A(B+h)^{1/2}$, with $A=2.2$ and $B=1.8$].
III. CHEMICAL DIFFUSION

We consider here mixed adlayers, where a mobile species, CO(ads), which hops to adjacent empty sites, coexists with an immobile species, O(ads). In the hydrodynamic regime of high CO-mobility, chemical diffusion is described in terms of the diffusive mass flux, \( J_{\text{CO}} \), of CO(ads) across the surface generated by spatially non-uniform coverages. We emphasize that a flux, \( J_{\text{CO}} \), is generated both by gradients in the CO-coverage, and in the O-coverage, so one writes

\[
J_{\text{CO}} = -D_{\text{CO,CO}} \nabla \theta_{\text{CO}} - D_{\text{CO,O}} \nabla \theta_{\text{O}},
\]

for small gradients. The coefficients \( D_{\text{CO,CO}} \) and \( D_{\text{CO,O}} \) are not generally constant, and below we explicitly determine their coverage dependence. We note that since diffusion is not possible for when \( \theta_{\text{CO}} + \theta_{\text{O}} = 1 \), and thus \( \nabla \theta_{\text{CO}} = -\nabla \theta_{\text{O}} \), it follows that \( D_{\text{CO,CO}} = D_{\text{CO,O}} \) for such a "jammed" surface.

For general lattice-gas models involving surface diffusion of all adspecies, a unique relationship of the form (3) between flux and coverage gradients only exists in the hydrodynamic regime of high mobility. Here, the diffusion coefficients are determined by the partial coverages (and substrate temperature), which determine the unique locally equilibrated steady state of the adlayer, although we emphasize that these coefficients depend on the spatial correlations within this state. [19] For our model, the situation is actually more complicated since in the locally "equilibrated" state, the distribution of immobile O(ads) depends on the history of formation of that state, rather than just on coverages. However, for
steady-state chemical wave propagation, there is in fact a unique local reactive state for each
point across the wave front. In addition to studies of the hydrodynamic regime, directly below
we also consider the case of finite mobilities, where there is some basis for the definition of
an effective chemical diffusivity.

A. Effective Chemical Diffusivity For Finite Mobility

From examination of exact master equations for spatially non-uniform system, it is
clear that spatial non-uniformities produce a diffusive flux of CO. For the square lattice, with
sites (i,j), suppose one has translational invariance in the j-direction. Then let $[O_i]$ denote the
mean O-coverage in column ‘i’, let $[E_i O_{i+1}]$ denote the probability of an adjacent empty site
in column ‘i’ and O-occupied site in column ‘i+1’, etc.. Then the net diffusive flux of CO(ad)
from column ‘i’ to column ‘i+1’ has the form [8]

$$J_{CO}(i\rightarrow i+1) = h([CO_i E_{i+1}] - [E_i CO_{i+1}]) = -h([CO_i E_{i+1}] - [CO_i]) + h([O_i CO_{i+1}] - [CO_O i+1]).$$ (4)

Since $a J_{CO}(i\rightarrow i+1) \rightarrow (J_{CO})_x$, $a^2 h \rightarrow D^0$ (the CO-diffusion coefficient for vanishing coverages),
and $a^{-1}([A_{i+1}] - [A_i]) \rightarrow \partial / \partial x$, for large h, if one neglects correlations in the occupancy of
adjacent sites, one obtains

$$(J_{CO})_x = -D^0(1-\theta) \frac{\partial \theta_{CO}}{\partial x} - D^0 \theta_{CO} \frac{\partial \theta_{CO}}{\partial x}$$ (5)
This expression has the qualitative form of eq.(3) above, although we emphasize that it is not exact, due to the neglect of spatial correlations (except when $\theta_0 \to 0$; see Sec.III.B).

From the simulation results of Sec.II, it is also clear that spatial non-uniformities are removed in the absence of adspecies hopping due to spatial coupling associated with nearest-neighbor adsorption site requirement for $O_2$, and the adjacent site requirement for reaction. This indirect adsorption-desorption (reaction) pathway produces a non-diffusive CO(gas) flux that is controlled by adsorption and reaction rates, and the range of the spatial coupling (here just one lattice spacing). As also noted in Sec.II, this phenomenon apparent in general Spatial Contact Models, [15] where the equations governing spatiotemporal behavior can be rewritten in a reaction-diffusion form within so called “diffusion approximation” (which also neglects spatial correlations). Specific analyses of this type for monomer-dimer reaction can be found in Ref.s [20,21]. These studies primarily utilize the simplest “site-approximation”, which neglects all spatial correlations. Generalization to more sophisticated “dynamic cluster” approximations, which account for short range correlations, is straightforward. [4,20,21] However, such approximations cannot accurately describe the strong spatial correlations and fluctuations, for small h. Of more significance is the observation that they generally cannot describe the non-trivial nature of chemical diffusion in mixed adlayers, for realistic large h. This is clearly the case for the model studied here where correct description of the percolative nature of diffusion requires a sophisticated characterization of the connectivity of non-O(ads) regions of the lattice.

Chemical diffusion coefficients cannot be precisely defined for finite hop rates. Since there is not a complete separation of time-scales for hopping (diffusion) and other processes,
relaxation of weak perturbations of uniform states will be dominated by non-diffusive pathways. However, it is natural to define an effective chemical diffusivity based, e.g., on the type of wave propagation behavior described in Sec.II. Since true diffusion and adsorption-desorption mechanisms provide parallel pathways for spatial homogenization, the total effective diffusivity is given by sum of contributions from these pathways, as is already apparent in the identification of $D_{\text{eff}}$ in Sec.II. However, we emphasize that the former contribution dominates in the hydrodynamic regime, which is of relevance to surface reactions.

B. Chemical Diffusion In Non-Interacting Lattice Gases

There is a special case where the analysis and properties of chemical diffusion are particularly simple, and which is of direct relevance to this study. This is the case of "random diffusion" of a non-interacting adspecies of finite coverage or "density" by hopping to adjacent vacant sites, either on a perfect lattice, or in a static disordered lattice where some sites are "blocked". Here, it is known that the associated many-particle master equations describing diffusion reduce to single-particle diffusion equations. [22,23] An important consequence is that the chemical diffusion coefficient, D, is independent of the coverage of the diffusing species. Of course, the diffusion of a single particle and, thus, the diffusion of the non-interacting lattice-gas, depends on the disordered environment.

The key results relevant to our study can be extracted from analyses of transport in lattice percolation models where some fraction, $q$, of the lattice sites are "impurities" which block transport. [24] We apply these results to analyze transport of the highly mobile adspecies CO, where the "impurities" correspond to coadsorbed O. The basic feature of these
models is that "percolating clusters" of neighboring vacant sites, which connect opposite sides of the system, exist only when \( q < q_c \). Thus, for \( q < q_c \), long-range diffusion (by hopping between adjacent vacant sites) is possible, and \( D > 0 \). For \( q > q_c \), no long-range diffusion is possible, and thus \( D = 0 \). If we set \( D = D^0 \) when \( q = 0 \), and write \( D = D^0 F_{perc}(q) \), then \( F_{perc}(q) \) decreases from unity (when \( q = 0 \)) to zero (as \( q \) increases to \( q_c \)), and \( F_{perc}(q) = 0 \), for \( q \geq q_c \). We emphasize that the critical percolation threshold depends on correlations in the distribution of the blocked sites. However, the nature of the non-linear disappearance of \( F_{perc}(q) - (q_c - q)^\mu \) upon approaching the critical threshold (from below) is described by a universal exponent \( \mu = 1.3 \). [24] We also note that most studies of percolation focus on connectivity of the occupied rather than the vacant sites. These are generally distinct problems, [25] one exception being the most commonly studied "ideal case" of randomly distributed blocked sites.

In this work, we shall also exploit another quantitative characterization of the dependence of \( D \) on \( q \), which is provided by formal "density" expansion techniques. [26] These expansions are obtained by first developing an Ursell-Mayer cluster expansion for (a suitable transform of) the propagator for diffusion on a disordered lattice. The \( m^{th} \) order term in this cluster expansion involves only propagators for lattices with up to \( m \) impurities, and this determines the \( q^m \)-term in the expansion \( D \), after appropriate ensemble average over relative positions of such finite subsets of impurities. To date, only the case of a random distribution of impurities has been considered, where such ensemble averages involve
uniform sums over all relative positions of subsets of m impurities. [26] In particular, for a square lattice, such an analysis yields [26]

\[ F_{\text{perc}}(q) = 1 - (\pi-1)q - \alpha q^2 + O(q^3). \]  \hspace{1cm} (6)

where \( \alpha = 0.85571 \). The quadratic approximation to eq.(6) reproduces simulation results with uniform accuracy, and produces an estimate for \( q_c \) of 0.4023 (corresponding to \( D=0 \)), which should be compared with the exact value of 0.4073. Of course, this approximation produces \( \mu=1 \), rather than the correct non-trivial value.

From the above discussion, it is clear that the introduction of spatial correlations in the (static) distribution of impurities does not change the linear “single impurity” term in eq.(6). However, the quadratic term is associated with sum over the relative position of pairs of impurities, which must now be weighted by the associated two-point probability distribution (rather than being a uniform sum). Thus \( \alpha \) is modified depending on this distribution. It is appropriate to note that this pair probability function provides somewhat indirect information on the percolation threshold, in contrast to the distinct pair connectivity function. [24] Thus, one should not expect the quadratic approximation to eq.(6), with appropriately calculated \( \alpha \), to accurately predict \( q_c \). However, our strategy will be to use a quadratic approximation with \( \alpha \) chosen to match an independently determined \( q_c \), and this expression is expected to uniformly approximate \( F_{\text{perc}} \).
C. Chemical Diffusion Coefficients $D_{CO,CO}$ And $D_{CO,O}$

In our monomer-dimer reaction model, the disordered environment through which the highly mobile non-interacting CO(ads) diffuses is provided by the immobile coadsorbed O(ads). Since the CO(ads) hop rate much higher than all other rates, this environment can be regarded as effectively static. Thus, the chemical diffusion coefficient, $D_{CO,CO}$, will depend on the coverage and configuration of the coadsorbed O(ads), but not on $\theta_{CO}$. Although, as noted above, the local state depends on its history of formation, rather than just on $\theta_O$ (and $\theta_{CO}$), it is instructive (but oversimplistic) to write

$$D_{CO,CO} = D^0 F_{perc}(\theta_O),$$

where again $D^0 = a^2 h$ is the CO-diffusion coefficient for vanishing coverages.

In analyzing the diffusive flux of CO(ads) induced by a gradient in the O(ads)-coverage, a key observation is that the many-particle master equations for the non-interacting CO lattice-gas still reduce to single-particle equations, even for a non-uniform disordered background. Thus, the induced flux must be directly proportional to the CO(ads)-coverage, and one can write $D_{CO,O} = D^0 \theta_{CO} G(\theta_O)$. Then the condition that $D_{CO,CO} = D_{CO,O}$ for a "jammed" surface, where $\theta_{CO} + \theta_O = 1$, yields $G(x) = F_{perc}(x)/(1-x)$, so

$$D_{CO,O} = D^0 \theta_{CO} F_{perc}(\theta_O)/(1-\theta_O).$$ (8)
Below we describe the prescription eq.(7) and eq.(8) as percolative CO-diffusion.

IV. HYBRID TREATMENT OF LIMITING BEHAVIOR FOR HIGH CO-MOBILITY

A. The Hybrid Mean-Field/Lattice-Gas Formalism

In the regime of high CO mobility (i.e., very large $h$), the adsorbed CO are locally randomized in a quasi-static disordered environment of coadsorbed O. For this reason, it is natural to analyze directly this limiting behavior within a so-called “hybrid” formalism. [8,27] Here, the immobile O(ads) distribution is treated within a lattice-gas (LG) framework (just as for any finite $h$), but the CO(ads) is described by a single mean-field parameter, $\theta_{CO}=\theta_{CO}(x,t)$, representing the local CO-coverage at a macroscopic point, $x$, at time $t$. For a spatially uniform system, where $\theta_{CO}=\theta_{CO}(t)$, analysis of this hybrid model reveals true bistability of reactive and CO-poisoned states over a range of $p_{CO}$ from $p_{s-}=0$ to $p_{s+}=0.500$. [8] Such true bistability is expected since increasing $h$ enhances metastability in the full LG model, as noted in Sec.I and II. We emphasize, however, that this hybrid model does not provide an exact analysis of $h\rightarrow\infty$ limiting behavior of the full LG model. For the latter, there are variations or fluctuations in the CO coverage on regions which are topologically disconnected by “walls” of O(ads). These fluctuations are not accounted for in the hybrid treatment. While there is no indication that they effect the qualitative behavior of the model, they could produce small quantitative changes.

In reality, $h$ is finite, although typically very large. Thus local equilibration (i.e., randomization) of CO(ads) is efficient, but there can be variations of CO (and O) coverages.
on a mesoscopic length scale, $O(h^{1/2})$. This feature is manifested in experimentally observed wave propagation and pattern formation. [1] To treat such phenomena within the hybrid approach, one can simulate in parallel the state of distributed macroscopic points with distinct local coverages, using a LG description of O(ads), and a MF description of CO(ads), with $\theta_{CO}$ now representing the local coverage. One must also suitably couple the evolution at these distinct macroscopic points (and thus of the parallel simulations) to describe the macroscopic diffusive mass transport of CO(ads). [8] Within such a "hydrodynamic" reaction-diffusion formalism, it is necessary to prescribe the chemical diffusivity of CO(ads). The simplest approximate treatment assumes a constant diffusion coefficient, and a modified treatment has been considered which accounts for the influence of coadsorbed species, but neglects all spatial correlations, i.e., using eq.(5) for $J_{CO}$. [8] However, for the model under consideration here, the appropriate non-trivial prescription of percolative diffusion is given by eq.s (7) and (8) in Sec.III.C.

Below, we exploit this hybrid treatment of spatially inhomogeneous systems to analyze the evolution of planar chemical waves. Paralleling the study of Sec.II, we examine the displacement of the reactive steady-state by the CO-poisoned state, which occurs for $p_{CO}$ below an equistability point in the bistability region. For $p_{CO}$ above this equistability point, the displacement would be reversed for constant $D$, but is actually absent for percolative diffusion (see Sec.IV.B). In any case, by scanning $p_{CO}$ across the bistability region, one can determine the equistability point for these two states. The equistability point corresponds to, and thus provides a direct estimate of $p^*(h->\infty)$, which was determined independently in Sec.II. [8,11]
B. Wave Propagation With Percolative Diffusion: General Properties

Within a hybrid formalism, planar chemical wave propagation in the \( x \)-direction is described by equations of the generic form [8]

\[
\frac{\partial}{\partial t} \theta_{\text{CO}} = p_{\text{CO}} \theta_{\text{E}} - 4k \theta_{\text{O,CO}} + \frac{\partial}{\partial x} \left[ D_{\text{CO,CO}} \frac{\partial}{\partial x} \theta_{\text{CO}} \right] + \frac{\partial}{\partial x} \left[ D_{\text{CO,O}} \frac{\partial}{\partial x} \theta_{\text{O}} \right],
\]

\[
\frac{\partial}{\partial t} \theta_{\text{O}} = 2p_{\text{O2}} \theta_{\text{EE}} - 4k \theta_{\text{O,CO}}.
\]

(9)

Here \( \theta_{\text{CO}} \), \( \theta_{\text{O}} \), and \( \theta_{\text{E}} = 1 - \theta_{\text{CO}} - \theta_{\text{O}} \) denote the probability that a site is occupied by CO, O, or empty (E), respectively, \( \theta_{\text{O,CO}} \) denotes the probability of finding an adjacent O-CO pair (as distinct from a CO-O pair), and \( \theta_{\text{EE}} \) denotes the probability of an adjacent empty pair. Since the CO(ads) are locally randomly distributed, one has \( \theta_{\text{O,CO}} = \theta_{\text{O2}} \theta_{\text{CO}} / \theta_{\text{Z}} \) and \( \theta_{\text{EE}} = \theta_{\text{ZZ}} (\theta_{\text{E}} / \theta_{\text{Z}})^2 \) where \( \text{Z} \) denotes a non-O site. We emphasize that since the O’s, and thus the Z’s, are not randomly distributed, these equations are not closed, and need to supplemented by an infinite hierarchy [8]. However, direct assessment of some of the properties of the solutions to eq.(9) is still possible. For a chemical wave with velocity \( V \), one has \( \theta_{\text{CO}} = \theta_{\text{CO}} (\xi = x - V t) \), etc., and the above equations (and their extended hierarchy) can be reduced to ordinary differential equations in the standard way upon making the replacements \( \frac{\partial}{\partial t} \rightarrow V \frac{\partial}{\partial \xi}, \frac{\partial}{\partial x} \rightarrow \frac{\partial}{\partial \xi} \). [18]

Consider first the case of \( p_{\text{CO}} \) below the equistability point (see Sec.IV.A) in the hybrid formalism, so that a planar chemical wave can be formed in which the reactive state on the left, say, displaces the CO-poisoned state on the right. This corresponds to \( V > 0 \). For
our reaction model, \( \theta_0 \) in such a reactive state always exceeds the critical threshold, \( q_c \), for
the termination of CO-diffusion, and trivially \( \theta_0=0 \) in the CO-poisoned state. Thus, \( \theta_0 \) will
decrease from above \( q_c \), to below \( q_c \), with increasing \( \xi \). Consequently, we can assign \( \xi=0 \) to
the point where \( \theta_0=q_c \), and then there is no CO-diffusion for \( \xi<0 \). Then, it is clear from the
above equations that the profile shape for \( \xi<0 \) is simply determined by the time-trace (after
the replacement \( t \rightarrow x/V \)) of the coverages in a uniform system relaxing from the state at \( \xi=0 \)
to the reactive steady-state. For \( \xi>0 \), the profile depends on the form of \( D_{CO,CO} \) and \( D_{CO,0} \).
One can show that when \( V>0 \), the profile is continuous, and there is no slope discontinuity at
\( \xi=0 \) since \( \mu>1 \). [28] However, upon approaching the equistability point, where \( V \rightarrow 0 \), the
profile develops a discontinuity at \( \xi=0 \): coverages approach their reactive steady-state values
for all \( \xi<0 \), so \( \theta_0 \rightarrow \text{constant strictly exceeding } q_c \); however, \( \theta_0 \) decreases from \( q_c \) to zero, for
increasing \( \xi \geq 0 \). This behavior is indicated schematically in Fig.4.

For \( p_{CO} \) just above the equistability point, propagation involving displacement of the
reactive steady-state by the more stable CO-poisoned state does not occur in this hybrid
formalism with percolative diffusion. This is because the reactive steady-state value of \( \theta_0 \)
exceeds \( q_c \), which precludes diffusive coupling of the CO-poisoned state to this reactive state.
(However, as \( p_{CO} \) approaches the upper spinodal, the reactive steady-state value of \( \theta_0 \) drops
below \( q_c \), and again propagation occurs.)

For comparison, we briefly describe corresponding behavior in the LG model for \( p_{CO} \)
just above \( p^* \). Since the metastable reactive steady-state value of \( \theta_0 \) also exceeds \( q_c \) in the LG
model, diffusive coupling of the CO-poisoned state to this metastable reactive state is again inhibited. On the other hand, direct spatial coupling between these states always exists due to reaction of neighboring CO and O adspecies, and, in fact, extensive "local diffusion" of CO(ads) from the CO-poisoned state into the "frontier" of the reactive state is possible. Thus the CO-poisoned state does displace the metastable reactive state (at least until the latter poisons). While we find that the interface propagation velocity and structure at first vary conventionally with increasing $h$, eventually the inhibited diffusive coupling must control behavior. A detailed analysis will be reported elsewhere.

C. Wave Propagation With Percolative Diffusion: Simulation Results

As an initial simplified treatment of wave propagation within the hybrid formalism, we assume that the "weak" correlations in the distribution of adsorbed O do not affect the percolation or transport properties for diffusing CO(ads). In this case, to describe chemical diffusion of CO(ads), one might use eq.s (7) and (8) with a quadratic approximation for $F_{\text{perc}}$, where we slightly adjust the value for $\alpha$ from Ref. [26] so that we recover exactly the random percolation threshold of $q_c=0.4073$. With this choice, we determine that the equistability point for the reactive and CO-poisoned states occurs at $p_{\text{CO}} = 0.395\pm0.001$.

Next, we implement a self-consistent treatment of percolation and transport within the hybrid formalism, as follows. In the above analysis of wave propagation near the equistability point, one can analyze the simulated distributions of adsorbed O across the wave front to assess at what position (and, thus, at what value of $\theta_0$) the non-O sites cease to percolate. Specifically, we use small-cell real-space renormalization group techniques [29] to estimate
Fig. 4 Schematic of the chemical wave profile for $p_{CO}$ slightly below $p^*$. 

- **$\theta_{O}$**
- **$\theta_{CO}$**
- **$q_c$**
- **profile corresponds to time trace**
- **profile reflects diffusion**
- **poisoned state**

**no diffusion**

**diffusion**

$\xi = 0$
the shift in the percolation threshold from its value for a random distribution. See Appendix C for more details. From this analysis, one finds that the percolation threshold is shifted upward from \( q_c = 0.4073 \), for random distributions, to \( q_c = 0.435 \), as might be expected for weakly clustered distributions. [30] With this revised estimate of \( q_c \), we appropriately refine our description of CO-chemical diffusion. Specifically, we use the quadratic approximation for \( F_{\text{perc}} \) in terms of \( \theta_0 \), but with an adjusted value of \( \alpha \) so as to obtain the appropriate \( q_c = 0.435 \). We then reanalyze wave propagation and equistability. One could then continue to reassess percolation across the wave front, revise the treatment of CO-diffusion, reanalyze equistability, etc., until achieving self-consistency. However, to the level of precision used here, \( q_c \) does not change significantly from the first revised estimate of 0.435, and we obtain a final estimate of \( p_{CO} \approx 0.398 \pm 0.001 \) for the position of equistability point. We emphasize that this result is consistent with the value of \( p^*(h \to \infty) = 0.397 \) from Sec.II.

It is instructive to compare the above results for the equistability point in the hybrid model with those obtained from corresponding simulations with other (imprecise) treatments of diffusion. Results are shown in the right column of Table II for standard diffusion (Constant D), an approximate treatment based on eq.(5) which underestimates the influence of coadsorbed O on CO-diffusion (Modified), a correct treatment of \( D_{CO,CO} \) which ignores the "off-diagonal" contribution due to \( D_{CO,0} > 0 \) (Diagonal), and the exact treatment above (Exact). For the latter two cases, we report results for random percolation with \( q_c = 0.407 \) (R), and for correlated percolation with \( q_c = 0.435 \) (C). In addition, Table II shows corresponding results from a "site-approximation" and a "pair-approximation" to eq.(9) and the associated
hierarchy. [8] The former ignores all spatial correlations, and corresponds to a standard MF
treatment, whereas the latter accounts for nearest-neighbor correlations. These results show
that the prescription of diffusion does significantly influence the location of the equistability
point, thus highlighting the importance of a correct treatment. They also show that the pair
approximation provides an adequate treatment of spatial correlations in this hybrid model (cf.
Ref.[8]).

Table 2. Estimates for the location of the equistability point of the monomer-dimer model in
the hydrodynamic regime. Results are shown for simulations of the hybrid model (Sim), and
for site- and pair-approximations of the master equations for this model. We also show the
dependence of these estimates on the prescription of diffusion. See the text.

<table>
<thead>
<tr>
<th></th>
<th>Site</th>
<th>Pair</th>
<th>Sim</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant D</td>
<td>0.4420</td>
<td>0.4401</td>
<td>0.440</td>
</tr>
<tr>
<td>Diagonal (R)</td>
<td>0.4159</td>
<td>0.4062</td>
<td>0.406</td>
</tr>
<tr>
<td>(H)</td>
<td>0.4175</td>
<td>0.4084</td>
<td>0.409</td>
</tr>
<tr>
<td>Exact (R)</td>
<td>0.4061</td>
<td>0.3945</td>
<td>0.395</td>
</tr>
<tr>
<td>(H)</td>
<td>0.4078</td>
<td>0.3970</td>
<td>0.398</td>
</tr>
</tbody>
</table>

Simulations or approximate analytic treatments of the hybrid model can also be used
to examine the variation of propagation velocity with $p_{CO}$, as well as the details of wave front
structure. Fig.5 shows results for the scaled velocity, $v=V/h^{1/2}$, obtained from simulations of
the full LG model with $h=512$, compared against predictions of the hybrid model with
Fig. 5 Scaled propagation velocity, $v$, of the chemical wave versus $p_{CO}$. Simulation results for the monomer-dimer LG model, with large $h=512$, are compared with predictions from the hybrid treatment with various prescriptions of chemical diffusion.
various treatments of diffusion (and with the identification $D^0 = a^2 h$, where ‘a’ is the lattice constant). Clearly a correct description of diffusion is necessary to quantitatively reproduce the value of the propagation velocity as well as the equistability point. In Fig.6a, we show results for the coverage profiles across the stationary wave front at the equistability point obtained from the correct description of percolative diffusion. The shape of the profiles is very similar to that obtained from the LG simulations for large $h$ shown in Fig.3c. On the other hand, the shape shown in Fig.6a is quite distinct from the smooth form obtained using a conventional description of chemical diffusion with constant $D$, which is shown for comparison in Fig.6b.

V. MODEL REFINEMENTS AND COMPARISON WITH EXPERIMENT

We emphasize that the monomer-dimer surface reaction model described above provides a highly idealized description of CO-oxidation. Realistic treatments must include a number of additional features, listed below, which will modify the kinetics, wave propagation, and chemical diffusion of CO(ads):

(i) Non-zero mobility of adsorbed O. Provided the hop rate for the CO(ads) is far higher than that for O(ads), the picture of CO(ads) diffusing in a *disordered quasi-static environment* of coadsorbed O remains valid. The chemical diffusion of CO(ads) is still described as above, and controls spatiotemporal behavior. In contrast, for systems involving coadsorbed species with comparable high mobility, the description of chemical diffusion is distinct and more complicated. [33]
Fig. 6 Hybrid-model simulations for coverage profiles across the interface between the reactive steady-state (on the left) and the CO-poisoned state (on the right) at the equistability point (corresponding to the discontinuous transition, $p_{CO}=p^*$, in the LG model) for: (a) percolative diffusion of CO; (b) standard diffusion of CO with constant D. Here $D_0=D(\theta_0=0)$. 
(ii) Adspecies interactions. Such interactions affect the adsorption and desorption (or reaction) kinetics, as well as producing nonlinearities in chemical diffusion. [19]

(iii) Non-reactive desorption of CO(ads). With any such desorption, the completely CO-covered lattice is no longer a steady state. Introducing small desorption rates, the discontinuous transition persists in the LG model with finite h. [34] Also, bistability persists in the hydrodynamic regime, although the lower spinodal becomes a saddle-node bifurcation rather than a transcritical bifurcation. However, this change has no affect on the qualitative nature of chemical diffusion or of wave propagation.

(iv) Other features. Experimental observations of CO adsorption on O-covered surfaces in some systems [1] indicates the possibility of distinct adsorption sites, and furthermore suggest that diffusion of CO(ads) will not be as inhibited by coadsorbed O(ads) as in our treatment. Adsorbate-induced reconstruction of the substrate is also important in a number of systems, and necessitates more complicated atomistic modeling.

Next we briefly comment on experimental observations of chemical wave propagation, and of the relevance of the current study. Photo-Emission Electron Microscopy (PEEM) studies have provided the most extensive data on chemical wave propagation, although these have not systematically measured V versus P_{CO}. [1] In any case, quantitative analysis of propagation velocities and extraction of surface diffusivities requires sophisticated treatment of non-linearities in chemical diffusion of the type described here. PEEM does not have the resolution to discern the type of features of wave front structure discussed here, but this is possible with Low Energy Electron Microscopy (LEEM) or Mirror Electron Microscopy (MEM). [35]
VI. SUMMARY

We have analysed chemical wave propagation in a lattice-gas monomer-dimer surface reaction model for CO-oxidation, for finite reaction rate and for various degrees of CO-mobility. A “near-crossing” feature of the propagation velocity versus $p_{CO}$ curves allows precise estimation of the position of the CO-poisoning transition in the physically relevant limiting regime of high CO-mobility. This estimate is consistent with a direct treatment of wave propagation in this limiting regime, within a “hydrodynamic” reaction-diffusion formalism, using a hybrid approach of Ref.[8], if one accounts for the percolative nature of CO chemical diffusion. However, it is not consistent with the estimate obtained using the traditional description with constant D. We also find that the shape of the wave profile close to the CO-poisoning transition is sensitive to the percolative nature of CO-diffusion, and quite distinct from predictions with constant D.

ACKNOWLEDGEMENTS

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APPENDIX A: MONOMER-DIMER MODEL WITH INSTANTANEOUS REACTION

Goodman et al [10] analyzed chemical wave propagation for the monomer-dimer reaction model with $infinite$ $k$, but retaining mobile CO(ads) with hop rate $h$, and immobile
O(ads). A “near-crossing” of $V$ versus $p_{CO}$ curves, for different $h$, was first observed in this model. Since the location of the CO-poisoning transition, $p^*(h)$, as well as $dV/dA$, increases with $h$, the “crossing point” occurs for $p_{CO} = p_x$ above $p^*(h)$. Just as for the case $k=1$, one can exploit this “near-crossing” behavior to estimate

$$p^*(h \to \infty) = p_x = 0.575, \text{ for infinite } k. \quad (10)$$

This result agrees with the prediction of Ref.[11] that $p^*$ should increase with $h$ from $p^*(0)=0.526$ to a value strictly below $2/3$, and contrasts earlier claims. [31]

Note that wave propagation for $p_{CO}>p^*$ (up to $ps^+$) corresponds to displacement of the stable CO-poisoned state by the metastable reactive state, and thus only occurs until the latter poisons. Wave propagation is not well-defined for $p_{CO}>ps^+$. Thus, for $k=\infty$, $V$ versus $p_{CO}$ curves must be extended into this “metastable propagation” regime above $p^*$ in order to reach the “crossing point”. In fact, this is not even possible for small $h<9/4$, where $p^*_x<p_x$, but is readily achieved in practice for larger $h$ due to strong metastability.

APPENDIX B: FLUCTUATIONS IN CHEMICAL WAVE PROPAGATION

As noted in Sec.III.C, the fluctuations in the location of the interface include both intrinsic and long-wavelength contributions. Precise definition of the former is generally vague. For $p_{CO}<p^*$, where the long-wavelength fluctuations are of the KPZ-type, the amplitude, $\xi_i$, of the intrinsic fluctuations can in principle be extracted from the total
amplitude, $\xi$, for a system of width $L$, from the asymptotic slope of $\xi^2/L = \xi^2/L + \gamma(24v)$ versus $1/L$. On the other hand, in the regime of large $h$ of interest here, the intrinsic fluctuations dominate on the characteristic length scale $L \sim h^{1/2}$ (recalling that $v \sim h$). Some insight into the behavior of $\xi$ in this regime comes from the analysis of "diffusion fronts" in non-reactive systems. Here it has been shown that the amplitude of fluctuations at the diffusion front (defined as the "sea-shore" of the diffusing species) scales like $(d\theta/dx)^{-4/7}$, where $d\theta/dx$ denotes the concentration gradient at the front. For our system, this gradient scales like $h^{-1/2}$, which suggests that $\xi \sim h^{3/7}$. As an aside, we note that Goodman et al [10] used the term "intrinsic width" in their study. This corresponds to our characteristic length, $L \sim h^{1/2}$, rather than to $\xi \sim h^{3/7}$.

APPENDIX C: REAL-SPACE RG ANALYSIS OF PERCOLATION

The real-space renormalization group (RG) procedure for estimating percolation thresholds [29] may be described as follows within the context of our study. We determine the probability, $R_Z$, for the non-$O$ sites (denoted by $Z$) in $b\times b$ cells to span the cell horizontally (say), as well as the coverage of $Z$-sites, $\theta_Z = 1 - \theta_O$, for various positions across the wave front near equistability. We thus obtain $R_Z$ versus $\theta_Z$, from which one can estimate the threshold, $\theta_O = 1 - \theta_Z = p_c$, above which percolation of the vacant sites ceases. Criteria for the threshold considered here include $R_Z = \theta_Z$ (for $b=3$), $R_Z = 1/2$ (for $b=3$), or $R_Z(b=2) = R_Z(b=3)$. For randomly distributed $O$-sites, these criteria yield $p_c = 0.3807, 0.4407, \text{ and } 0.379$, respectively, compared to the exact value of 0.4073. In this study, we apply the same
procedure for correlated distributions to estimate the shift, $\delta p_c$, in $p_c$ from its value for random percolation. We expect that the estimate of the shift is more accurate than that of the absolute value.

As a controlled test of this hypothesis, we consider irreversible Random Sequential Adsorption of O-dimers on adjacent sites of a square lattice. [25] For the three criteria listed above, one finds that $\delta p_c = 0.039, 0.025, 0.021$, respectively, compared with the exact value of $\delta p_c = 0.027$. [25] Based on this test, we have applied the criteria $R_z = l/2$ in our analysis (described in Sec.IV) of the percolation properties of Z-sites in the hybrid treatment of the monomer-dimer reaction model.

REFERENCES


[13] For comparison with results for this model, note that h in Ref.[8], and Γ in Ref.[9], denote the total hop rate for CO, rather than the hop rate per direction (as used here). Our results are not consistent with those in Ref.[9] for p* versus Γ.

[14] V also decreases linearly with Δ in the monomer-dimer model with infinite k. [6,10] However a non-linear decrease applies approaching a continuous poisoning transition. [6]


[23] The classic analysis of Kutner [22] for a non-interacting lattice-gas on a perfect lattice can be readily extended to the case of a (static) disordered lattice. See R. Kutner and K.W.


[28] Eq.(9) shows that the slope discontinuity, \( \frac{d}{d\xi} \theta_{CO}(0^+) - \frac{d}{d\xi} \theta_{CO}(0^-) \) must be matched by the \( \xi=0^+ \) value of \( -V^{-1} \frac{d}{d\xi} \left[ D_{CO,CO} \frac{d}{d\xi} \theta_{CO} + D_{CO,O} \frac{d}{d\xi} \theta_{O} \right] \), which is proportional to \( \text{F}_{\text{perc}}'(p_c) \). The exact value of \( \text{F}_{\text{perc}}'(p_c) \) is zero since the critical exponent \( \mu>1 \), but its value is nonzero it does occur using a quadratic approximation.


CHAPTER 7: AUTOCATALYTIC REMOVAL OF UNSTABLE NO+CO ADLAYERS: CHEMICAL DIFFUSION AND WAVE PROPAGATION IN A LATTICE-GAS MODEL

A paper in preparation for submission to the Journal of Chemical Physics
M. Tammaro and J. W. Evans

I. INTRODUCTION

A rich variety of spatiotemporal behavior has been observed in catalytic surface reactions: wave propagation in bistable systems, spiral formation in excitable systems, etc. [1] These patterns result from the interplay between non-linear reaction kinetics and chemical diffusion of adspecies. Large hop rates of some mobile species produce mesoscopic characteristic lengths and propagation velocities. Behavior is usually analyzed by mean-field (MF) reaction-diffusion (RD) equations. This technique has had considerable success despite the neglect of adlayer ordering which can influence both the reaction kinetics and the chemical diffusivity.

A specific subclass of such phenomena is associated with the autocatalytic removal of unstable adlayers of mixed reactants. One such example is NO-reduction by some coadsorbed reactant subsequent to dissociation of NO, which requires an adjacent empty adsorption site. [2] In the simplest situation, where adspecies adsorption or non-reactive desorption are absent, a surface which is completely covered by a mixture of NO(ads) and other reactants is
in an unstable steady state, due to the lack of empty adsorption sites required for NO-dissociation. However creation of empty sites or regions (e.g., via non-reactive desorption either homogeneously or at defects) can initiate dissociation of NO, and subsequent reaction. This leads to further autocatalytic creation of empty sites via subsequent dissociation and reaction. As a result, depending on the conditions, one could anticipate an “explosion” in the catalytic reaction rate. One can also envisage waves of transition from the unstable covered surface to some lower coverage state of excess reactant.

For a more general situation incorporating adsorption and non-reactive desorption of NO and reducing agent, one often still finds a metastable or an unstable steady state corresponding to the unreactive surface mostly covered by NO(ads) and other reactants. However, there may also exist a more stable reactive state (e.g., the oscillatory state in the NO+CO reaction). This more stable state can displace the unreactive state producing wave propagation.[2] Near the front of such a wave one would expect that the dominant processes are NO dissociation and reaction. Since behavior in this region presumably determines the propagation velocity of the wave, its behavior might be elucidated with simpler model excluding adsorption and desorption. In the wake of the pulse, development of the reactive state is obviously controlled by adsorption and desorption processes.

Similar situations exist where unreactive surface covered by NO(ads) and other reactants is actually stable, but the system is “excitable”. Such excited pulses of reaction travel through the NO+CO covered surface.[2] Near the front of the pulse, we expect that the dominant processes are NO dissociation and reaction, so propagation behavior might again be
elucidated with the simpler model. In the wake of the pulse, recovery to the NO+CO covered surface is obviously controlled by adsorption and desorption.

It is useful to develop a realistic atomistic lattice-gas (LG) model treatment of such surface explosions and wave propagation associated with the removal of unstable mixed adlayers. We emphasize that it is essential to incorporate realistic (high) hop rates for the more mobile adspecies. These are typically orders of magnitude larger than other rates associated with the reaction process. There is motivation to avoid apriori assumptions and approximations of standard MF RD equation treatment. In fact, a LG model allows examination of these assumptions, and development of exact RD formulation of behavior of the LG model in the "hydrodynamic regime" of high diffusivity. In this respect, the main issue for the model considered here is the appropriate description of non-linearities in the chemical diffusion in mixed adlayers.

In section II, we describe the NO+CO model. Then, in section III, we describe general chemical diffusion and how it is implemented in the NO+CO model. The mean-field reaction-diffusion equation analysis is described in section IV. Section V describes, in detail, the triggering of the NO+CO reaction from a small patch of empty sites. Finally, in section VI, we describe planar front propagation in the NO+CO model, and present results from simulations and reaction-diffusion equations for the chemical wave velocity, and wave profiles.
II. NO+CO REACTION MODEL WITHOUT ADSORPTION & DESORPTION OF REACTANTS

Here we describe a simple lattice-gas model for NO-reduction by CO on a Pt(100) surface pre-covered by a mixture of NO and CO. In our model we represent the surface with a 2-D square lattice. The steps in the reaction are as follows:

\[
\begin{align*}
\text{NO(ad)} + \text{E} & \rightarrow \text{N(ad)} + \text{O(ad)} \\
\text{CO(ad)} + \text{O(ad)} & \rightarrow \text{CO}_2(\text{g}) + 2\text{E} \\
\text{N(ad)} + \text{N(ad)} & \rightarrow \text{N}_2(\text{g}) + 2\text{E}
\end{align*}
\]

Here (ad) represents an adsorbed molecule, (g) a molecule in the gas phase and E an empty surface site. The first step represents the spontaneous dissociation of NO(ad) at rate $k_{\text{NO}}$ per adjacent empty site. The second step is the reaction between CO(ad)-O(ad) pairs at rate $k_{\text{CO+O}}$ per pair. The third step is the recombinative desorption of N(ad)-N(ad) pairs at rate $k_N$ per pair. We use the experimental values [3] for rates on Pt(100) at 400K of $k_{\text{CO+O}}=1.1\text{s}^{-1}$, $k_{\text{NO}}=0.13\text{s}^{-1}$, and $k_N=0.03\text{s}^{-1}$. In this model there is no adsorption or desorption of reactant species, and adspecies interactions (other than reaction) are ignored. We also allow hopping of adsorbed species to adjacent empty sites at rates $h_{\text{NO}}$, $h_{\text{CO}}$, $h_N$, and $h_O$ (per adjacent empty site) for NO(ad), CO(ad), N(ad), and O(ad) respectively. In this paper we report results only for $h_{\text{NO}}=h_{\text{CO}}=h_N=h$ and $h_O=0$. We are interested in the regime where $h \gg 1$, corresponding to
typical experimental situations where hop rates can be many orders of magnitude greater than other rates.

We consider the situation where the surface is initially covered with a uniform, random mixture of NO(ad) and CO(ad) such that $\theta_{\text{NO}} + \theta_{\text{CO}} = 1$. Since NO(ad) and CO(ad) do not react, and there are no empty sites for NO(ad) to dissociate, this is a steady state. Then we introduce a small number of empty sites. This allows NO(ad) to dissociate, creating CO(ad)-O(ad) and N(ad)-N(ad) pairs, initiating the reaction steps, leaving still more empty sites. Clearly the state of a completely NO-CO covered surface is unstable. The triggering of the "surface explosion" is discussed in detail in section V and planar front propagation is discussed in section VI. Next we describe, in detail, the properties of chemical diffusion in the NO-CO model.

III. CHEMICAL DIFFUSION IN THE NO-CO REACTION MODEL

First consider chemical diffusion in a mixed adlayer of NO(ad), CO(ad), N(ad), and O(ad). The diffusive flux of one species depends on the concentration gradients of all species, so one writes with complete generality,

\[
\begin{pmatrix}
\mathcal{J}_{\text{NO}} \\
\mathcal{J}_{\text{CO}} \\
\mathcal{J}_{\text{N}} \\
\mathcal{J}_{\text{O}}
\end{pmatrix} =
\begin{pmatrix}
D_{\text{NO,NO}} & D_{\text{NO,CO}} & D_{\text{NO,N}} & D_{\text{NO,O}} \\
D_{\text{CO,NO}} & D_{\text{CO,CO}} & D_{\text{CO,N}} & D_{\text{CO,O}} \\
D_{\text{N,NO}} & D_{\text{N,CO}} & D_{\text{N,N}} & D_{\text{N,O}} \\
D_{\text{O,NO}} & D_{\text{O,CO}} & D_{\text{O,N}} & D_{\text{O,O}}
\end{pmatrix}
\begin{pmatrix}
\nabla \theta_{\text{NO}} \\
\nabla \theta_{\text{CO}} \\
\nabla \theta_{\text{N}} \\
\nabla \theta_{\text{O}}
\end{pmatrix}.
\] (1)
The entries of the 4x4 matrix are the chemical diffusion coefficients and are not, in general, constant. For our NO+CO model where \( h_{\text{NO}} = h_{\text{CO}} = h_{\text{N}} = h \) and \( h_{\text{O}} = 0 \), it is possible to determine the exact form of the entries. Trivially, all entries in the bottom row are zero, due to the immobility of \( O(\text{ad}) \). Below we set \( D_0 = a^2 h \), where 'a' is the lattice constant.

To elucidate the complicated case above, it is useful to consider first the chemical diffusion in a mixed adlayer of two species, A and B. Again, one writes

\[
\begin{pmatrix}
1_A \\
1_B
\end{pmatrix} =
\begin{pmatrix}
D_{AA} & D_{AB} \\
D_{BA} & D_{BB}
\end{pmatrix}
\begin{pmatrix}
\nabla \theta_A \\
\nabla \theta_B
\end{pmatrix}.
\]

We will focus on the diffusion of A and consider two cases: (I) A is mobile and B is immobile such that \( h_A = h \) and \( h_B = 0 \); (II) A and B are both mobile and have the same hop rate, \( h_A = h_B = h \).

(I) Immobile B: In the first case, where \( h_A = h \) and \( h_B = 0 \), A diffuses through a static disordered environment created by the coadsorbed species B. Since there are no interactions between adspecies, it is possible to show that the master equations for diffusion of species A reduce to single-particle equations.[4,5] Thus, the chemical diffusion coefficient, \( D_{AA} \), is identical to the single-particle diffusion coefficient. Furthermore, the theory of (single-particle) transport in percolative systems applies to show that \( D_{AA} = D_{\text{perc}}(\theta_B) \) decreases with increasing \( \theta_B \) from \( D_0 \), when \( \theta_B = 0 \), to zero at the percolation threshold, \( \theta_B = \theta^* \), where paths of sites not occupied by B cease to connect opposite sides of the system.[6] Behavior near the threshold is described by universal exponents, but \( \theta^* \) and \( D_{AA} \) depend on the details of the
correlations in the B adlayer. Except for \( \theta_B \) close to \( \theta^* \), one can show that [7] for random percolation \( D_{\text{perc}}(\theta_B) = D_0[1-(\pi-1)\theta_B-\alpha\theta_B^2] \), where \( \alpha = 0.771 \).

The diffusive flux of A due to a gradient in the coverage of the disordered "static" background of coadsorbed B is accounted for in \( D_{\text{AB}} \). Since the master equations for diffusion of A reduce to single-particle equations, even for a non-uniform background of B, the magnitude of this flux must be proportional to \( \theta_A \). Thus one can write \( D_{\text{AB}} = \theta_A G(\theta_B) \). To determine \( G(\theta_B) \), consider a "jammed" surface where \( \theta_A + \theta_B = 1 \), so that \( \nabla \theta_A = -\nabla \theta_B \). Since here \( J_A = 0 \), it follows that \( D_{\text{AA}} = D_{\text{AB}} \) and \( G(\theta_B) = D_{\text{perc}}(\theta_B)/(1-\theta_B) \).

**(II) Mobile B:** In the second case, when \( h_A = h_B \), analysis is more difficult. Here the total coverage must satisfy the classic diffusion equation for a non-interacting single-species lattice-gas[5] with hop rate \( h \), so it follows that \( D_{\text{AA}} + D_{\text{BA}} = D_{\text{AB}} + D_{\text{BB}} = D_0 \). Furthermore, if \( D_{\text{AA}} = D(\theta_A, \theta_B) \), then by symmetry \( D_{\text{BB}} = D(\theta_B, \theta_A) \), so all entries are determined by the single function \( D(x, y) \) which we now characterize. In the limit \( \theta_A \to 0 \), \( D(0, \theta_B) = D(\theta_B) = D_0(1-\theta_B)f(\theta_B) \) reduces to the conventional tracer diffusion coefficient for a particle in a bath of particles with the same hop rate, where the "correlation factor"[8] satisfies

\[
f(x) = 1 - 0.621x + 0.087x^2 \text{ (see Appendix A). At jamming, where } \theta_A \to 1-\theta_B, \text{ one has}
\]

\[
D_{\text{AA}} = D_{\text{AB}} = D_{\text{BB}}, \text{ so } D(1-\theta_B, \theta_B) + D(\theta_B, 1-\theta_B) = D_0, \text{ indicating that } D(1-\theta_B, \theta_B) = D_0(1-\theta_B). \text{ It just remains to interpolate between these limits, which can be done exactly in this special case. From Ref. [9] we have}
\[ D(\theta_A, \theta_B) = D_{ir}(\theta) + \frac{\theta_A (D_0 - D_{ir}(\theta))}{\theta}, \quad (3) \]

where \( \theta = \theta_A + \theta_B \).

Now we return to determination of the diffusion coefficients for the full NO+CO problem. Suppose first that \( \theta_O = 0 \) so there are only three species present, all mobile with the same hop rate. Consider the diffusion of CO(ad). Our generic treatment of two species diffusion in case (II) is trivially generalized to cover this situation by identifying \( \theta_A = \theta_{CO} \) and \( \theta_B = \theta_{NO} + \theta_N \). Letting \( \theta = \theta_{CO} + \theta_{NO} + \theta_N \), we have

\[ J_{CO} = -D_{ir}(\theta)\nabla \theta_{CO} - \frac{\theta_{CO} (D_0 - D_{ir}(\theta))}{\theta} (\nabla \theta_{CO} + \nabla \theta_{NO} + \nabla \theta_N) \quad (4). \]

Similar expressions apply for \( J_{NO} \) and \( J_N \).

Now consider the effect of some immobile O(ad) in the system. By making a few simple observations, it is possible to generalize (4) as follows. The mobile species are diffusing on a surface "reduced" in area by a factor of \( (1 - \theta_O) \). Define a local coverage as a coverage divided by \( (1 - \theta_O) \) so, for example, \( \theta_{loc} = \frac{\theta_{CO} + \theta_{NO} + \theta_N}{(1 - \theta_O)} \). Next, since the total coverage of the three mobile species behaves like the A species in case (I), there must be a linear dependence on each term on \( D_{perc}(\theta_O) \). Thus, we redefine the tracer diffusion
coefficient so $D_r(\theta) \rightarrow D_r^\theta(\theta^{loc}) = D_{\text{perc}}(\theta) (1 - \theta^{loc}) f^\theta(\theta^{loc})$, where the correlation factor must be adjusted to account for the immobile O(ad) such that $f(\theta) \rightarrow f^\theta(\theta^{loc})$ (See Appendix A). To account for the effect, on CO(ad) for example, due to the gradient in the immobile O(ad), add a term analogous to $D_{AB}$ in case(I) with $\theta_A = \theta_{CO}$ and $\theta_B = \theta_O$. Finally, one obtains

$$J_{CO} = -D_r^\theta(\theta^{loc}) \nabla \theta_{CO} - \frac{\theta^{loc}_{CO} (D_{\text{perc}}(\theta) - D_r^\theta(\theta^{loc}))}{\theta^{loc}} (\nabla \theta_{CO} + \nabla \theta_{NO} + \nabla \theta_{N})$$

which accounts for all the entries in the second row of the 4x4 diffusion matrix. Similar expressions apply for $J_{NO}$ and $J_N$.

IV. MEAN-FIELD REACTION-DIFFUSION FORMALISM

Now we describe the mean-field reaction-diffusion equation analysis of the NO+CO model. Here, where correlations are ignored, the reaction-diffusion equations are

$$\frac{\partial \theta_{CO}}{\partial t} = -4k_{CO+O}\theta_{CO}\theta_{O} - \nabla J_{CO}, \quad \frac{\partial \theta_{NO}}{\partial t} = -4k_{NO}\theta_{NO}\theta_{E} - \nabla J_{NO},$$

$$\frac{\partial \theta_{O}}{\partial t} = -4k_{CO+O}\theta_{CO}\theta_{O} + 4k_{NO}\theta_{NO}\theta_{E}, \quad \frac{\partial \theta_{N}}{\partial t} = -4k_{N}\theta_{N} + 4k_{NO}\theta_{NO}\theta_{E} - \nabla J_{N},$$
where $\theta_J$ is the fraction of the surface covered with species $J$ (empty if $J=E$). The
dissociation, desorption, and reaction terms are readily identified and the fluxes are obtained
from the expressions in the previous section. These equations can be integrated using
standard numerical techniques [10], and results are presented below.

V. TRIGGERING THE REMOVAL OF UNSTABLE NO+CO ADLAYERS

Here we describe the triggering of the NO-CO adlayer removal by a small patch of $N_0$
empty sites. Imagine an isolated cluster of $N_0$ empty sites on an otherwise NO-CO covered
surface. Because of the high hop rate, these empty sites will quickly disperse, becoming
isolated empty sites. Now NO(ad), CO(ad), and N(ad) have the same hop rate. Thus as long
as the empty sites are isolated, and surrounded by these species, they will randomly diffuse
with the same hop rate. For each empty site, after a time $\sim 1/k_{NO}$ an adjacent NO(ad) will
dissociate. If at least one of the nearest neighbors of the O(ad) thus created is a CO(ad), then
a pair of empty sites is created, due to reaction, after an additional time $\sim 1/k_{CO+O}$. Because of
the high hop rate, these empty sites will rapidly diffuse away from each other and again
become isolated empty sites. In this picture, isolated empty sites diffuse at rate $h$, giving
birth to other empty sites at rate $1/\tau$, with $\tau = 1/k_{NO} + 1/k_{CO+O}$, where the exact value of $\tau$
depends upon the fraction, $\theta_{NO}$, of the surface covered with NO(ad). As long as $h \gg 1/\tau$, and
the concentration of empty sites is low, to a good approximation the total number of empty
sites is $N_0 e^{\tau t}$. Also, in this limit, the probability distribution for all empty sites, regardless
of when they were created, is identical to that of the original empty site. Therefore the probability density (or coverage $\theta_E$) of empty sites is, in the continuum limit, just the number of empty sites times the probability density of the first empty site. If $r$ is the distance from where the cluster of empty sites was at $t=0$, then

$$\theta_E(r,t) = \frac{N_0 e^{-rt}}{4\pi D t} \exp \left( -\frac{r^2}{4Dt} \right)$$  \hspace{1cm} (7)$$

Here $D \propto a^3 h$ is an effective diffusion coefficient for empty sites. Equation (7) is valid only at the beginning stages of the explosion, when $N_0 e^{-rt}/4\pi D t \ll 1$.

It is possible to calculate $\tau$ exactly in the MF limit by writing down the rate-equations for the number of $O(ad)$ and empty sites at the beginning stages,

$$\frac{dN_E}{dt} = -4k_{NO} \theta_{NO} N_E + 2(3k_{CO+O}) \theta_{CO} N_O$$

$$\frac{dN_O}{dt} = 4k_{NO} \theta_{NO} N_E - 3k_{CO+O} \theta_{CO} N_O$$  \hspace{1cm} (8)$$

The factor of 3 in the top equation occurs because when an NO(ad) dissociates, one site adjacent to the O(ad) created is guaranteed to be an N(ad). This leaves only three possible neighboring sites where a CO(ad) could be. This closed set of equations can be solved
exactly to show that $\tau = \frac{4k_{\text{NO}}\theta_{\text{NO}} + 3k_{\text{CO+O}}\theta_{\text{CO}}}{12k_{\text{NO}}k_{\text{CO+O}}\theta_{\text{NO}}\theta_{\text{CO}}}$, with $\theta_{\text{NO}} + \theta_{\text{CO}} = 1$. It is also possible to calculate D. Since the rate at which a diffusing empty site is filled, due to NO(ad)
dissociation, is $4k_{\text{NO}}\theta_{\text{NO}}$, and the rate at which the O(ad) created reacts with a CO(ad) is $3k_{\text{CO+O}}\theta_{\text{CO}}$, the hop rate of empty sites is effectively reduced such that

$$D = a^2\frac{4k_{\text{NO}}\theta_{\text{NO}}}{3k_{\text{CO+O}}\theta_{\text{CO}} + 1}.$$

In a full analysis of the surface explosion, one would use (7) for some “short time”, t, as the “initial” conditions for the reaction-diffusion equations. Eventually a circular reactive region forms, which propagates outward. As the circular reaction front propagates outward, it becomes asymptotically planar with constant velocity. In this limit, it suffices to consider the propagation of a planar front ahead of which is the unstable NO+CO covered surface, in the wake of which is any excess reactant [i.e., O(ads) if $\theta_{\text{NO}} > \theta_{\text{CO}}$, and CO(ads) if $\theta_{\text{NO}} < \theta_{\text{CO}}$]. (See Figs.1 and 2)

In a real system, with finite terraces, the removal of the NO-CO adlayer may not always be achieved through simple reaction front propagation. If the hop rate is very high, and the system is small enough, the vacancies will disperse to the boundary of the system before a reaction front forms. In this case the removal mechanism is a homogeneous reactive state. Another possibility is that instead of a single empty site or patch of sites acting as the triggering “center”, there are many such “centers” distributed over the surface. If the hop rate is high enough and they are not too far separated, once again a homogeneous reactive state will develop, without front propagation. However, if they are far enough apart and the hop
Fig. 1 Simulated configurations for the beginning stages of the reaction. Initial conditions are a pair of empty sites on an otherwise NO-CO covered surface. Unphysical h=1 is used here.

Symbols represent O=NO(ad), •=O(ad), ◦=CO(ad), and ▲=N(ad): (a) $\theta_{NO}=0.7$; (b) $\theta_{NO}=0.5$; (c) $\theta_{NO}=0.3$. 
Fig. 2 Simulated configurations of the NO-CO model with $h=10$ and $\theta_{NO}=0.7$. To highlight the removal of the NO-CO adlayer, only NO(ad) and CO(ad) are shown, with the same plot symbol: (a) a spreading circular reaction front; (b) a planar reaction front.
rate is low enough, circular reaction fronts will form and expand, eventually colliding with the other expanding fronts. Below we analyze the removal of the NO-CO adlayer by considering only planar front propagation.

VI. REMOVAL OF NO+CO ADLAYERS VIA REACTION FRONT PROPAGATION

Here we consider the removal of the NO-CO adlayer via planar reaction front propagation. We have performed simulations of the NO+CO reaction model to study the propagation of a planar reaction front. The initial conditions are an MxN (typically 800x1200) lattice completely covered with a random mixture of NO(ad) and CO(ad). To initiate the reaction, several rows on one boundary of the lattice are vacated. After a transient period, a reaction front forms and propagates across the surface at constant velocity. (Fig.3) The parameters in the simulation are the initial concentration of NO(ad) on the surface and the hop rate, h. Since the chemical wave velocity scales like \( V \sim h^{1/2} \), it is appropriate to define a scaled velocity, \( \nu = \frac{V}{h^{1/2}} \), which is finite in the hydrodynamic limit, \( h \gg 1 \). We have measured the velocity of the planar reaction front versus the initial concentration of NO(ad) [or equivalently CO(ad)] on the surface. We found that there is a slow convergence, in h, to the hydrodynamic limit. Therefore to measure the scaled velocity, we extrapolated data for finite h to \( h \to \infty \) via plotting \( \nu \) versus \( 1/h^{1/2} \). [11] We have also analyzed the reaction-diffusion equations to determine the scaled velocity and concentration profiles using various prescriptions for diffusion. In Fig.4, we show "exact" simulation results for the scaled velocity \( \nu = \frac{V}{h^{1/2}} \), for a range of \( \theta_{NO} \), as well as predictions from various MF reaction-
Fig. 3 Simulated configuration of a planar reaction front with $\theta_{NO}=0.5$ and $h=40$. The NO-CO covered region is at the bottom. Symbols represent $O=NO(\text{ad})$, $\bullet=O(\text{ad})$, $\otimes=CO(\text{ad})$, and $\blacktriangle=N(\text{ad})$. 
Fig. 4 Scaled chemical wave velocity from the simulation and the reaction-diffusion equations using various prescriptions for the diffusion coefficients.
diffusion equation analyses. Such an analysis for the standard description of diffusion (with $D_{CO}=D_{NO}=D_N=a^2h$) predicts a velocity substantially higher than the exact result. This is expected since the interference of coadsorbed species on diffusion is ignored. For the reaction-diffusion equations it was necessary to extrapolate, in time, in order to determine the asymptotic chemical wave velocity. (See Appendix B)

Along with the "standard" and "exact" treatments of diffusion, we also analyzed a "modified" diffusive flux where all correlations are ignored. [11] In a mixed adlayer of two species, A and B, one has for the flux of A,

$$J_A = -D_0((1-\theta_B)\nabla\theta_A + \theta_A \nabla\theta_B). \quad (9)$$

This equation treats the B as a randomized, (highly) dynamic background through which A diffuses. Although the "modified" and "exact" treatments give similar results, they are shown to differ for other models, the latter being more accurate. [12]

Fig. 5 shows the concentration profiles for simulations. Note that there is no significant build up of O(ad) in the wake of the reaction front unless $\theta_{NO}>0.5$. Even when there is a significant build up of O(ad) the percolative nature of the diffusion has a negligible effect on the velocity. This is because the O(ad) build up is in the wake of the chemical wave, whereas the velocity is controlled by the highly reactive front portion. Another feature of the profiles in Fig. 4 is the long tail of N(ad) behind the wave. The small value of $k_N$ is responsible for the slow removal of the N(ad), and unless the O(ad) coverage in the wake is
Fig. 5 Concentration profiles from simulations: top to bottom, $\theta_{NO}=0.3, 0.5, 0.7$. 
above the percolation threshold, the N(ad) will react away completely. In Fig. 6 are the corresponding wave profiles from the RD analysis, using the exact treatment of diffusion, as described in section III. The profiles in the simulation and all treatments of diffusion show very little differences.

APPENDIX A: TRACER DIFFUSION IN DISORDERED SYSTEMS

Equation (5) is not exact only in that $f^{\theta_o}(\theta^\text{loc})$ and $D_{\text{perc}}(\theta_o)$ are not known exactly. The quadratic approximation to $D_{\text{perc}}(\theta_o)$ is shown to reproduce simulation results with uniform accuracy [12], and in the limit that $\theta_o \to 0$, our quadratic approximation to $f^{\theta_o=0}(\theta)$ is accurate as well (See Fig. 7). However, when there is a nonzero concentration of immobile O(ad), the correlation factor does not necessarily remain unchanged. To assess the deviation from its value when $\theta_o=0$, we measured the tracer diffusion coefficient [8] of a mobile species, with local coverage $\theta^\text{loc}$, through an immobile background, with coverage $\theta_o$, which we assume has the form

$$D_{\text{perc}}(\theta^\text{loc}) = D_{\text{perc}}(\theta_o)(1-\theta^\text{loc})f^{\theta_o}(\theta^\text{loc}).$$  \hspace{1cm} (10)

We ran simulations and used (10) to extract $f^{\theta_o}(0.5)$. To determine the correlation factor as $\theta^\text{loc} \to 1$, we used $f^{\theta_o}(1) = \frac{1+\langle \cos \varphi \rangle}{1-\langle \cos \varphi \rangle}$, where $\varphi$ is the angle between successive jumps of the tracer. This is the usual expression for the correlation factor in the $\theta^\text{loc} \to 1$ limit [8,13].
Fig. 6 Concentration profiles from RD analysis: top to bottom, $\theta_{NO}=0.3, 0.5, 0.7$. 
Fig. 7 Analysis of the correlation factor: Solid circles represent simulation data for the correlation factor when \( \theta_0 = 0 \). Lines represent quadratic approximations of the correlation factor for various \( \theta_0 \). Top to bottom: \( \theta_0 = 0, 0.1, 0.2, 0.3 \) and 0.407 (percolation threshold).
Although this expression was derived for \( \theta_0 = 0 \), it matches our simulations accurately for all \( \theta_0 \geq 0 \). To obtain an expression for \( f^{\theta_0}(\theta^{\text{loc}}) \) we first assume that

\[
f^{\theta_0}(\theta^{\text{loc}}) = 1 + \alpha(\theta_0)\theta^{\text{loc}} + \beta(\theta_0)\theta^{\text{loc}}^2.
\]

Using quadratic approximations to \( f^{\theta_0}(1) \) and \( f^{\theta_0}(0.5) \) and \( f^{\theta_0=0}(\theta) = 1 - 0.621\theta + 0.087\theta^2 \) we determined that

\[
\alpha(\theta_0) = -0.621 - 1.150\theta - 1.000\theta^2 \quad \text{and} \quad \beta(\theta_0) = 0.087 + 0.432\theta + 0.610\theta^2.
\]

**APPENDIX B: DETERMINATION OF THE ASYMPTOTIC SCALED VELOCITY**

It is worthwhile to note here that, in the reaction-diffusion analysis, we observed a slow convergence in time for the reaction front to achieve constant velocity. For comparison with another unstable model, we analyzed front propagation in a single species "contact" model that is governed by

\[
\frac{\partial \theta}{\partial t} = -4k\theta(1-\theta) + D\nabla^2 \theta.
\]

In this model a single species will desorb at rate \( k \) per empty nearest neighbor. Again, a completely covered surface is an unstable steady state, and planar reaction front propagation can be studied. In this model, the asymptotic scaled is known to be \( 4(kD)^{1/2} \) exactly. We determined that the velocity approaches its asymptotic value like \( 1/t^\gamma \), with an exponent \( \gamma = 1 \). We used the same scaling exponent in the RD analysis to determine the asymptotic scaled velocity for the NO+CO model. (Fig.8) The simulations did not show the same slow convergence, but presumably they would have if \( h \) was large enough.
Fig. 8 Extrapolation of the scaled velocity used to determine its asymptotic value. Here $\theta_{NO} = 0.5$. 
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CHAPTER 8. GENERAL CONCLUSIONS

This thesis was concerned with the theoretical study of chemical reactions on metal surfaces. These systems are far-from-equilibrium, so classical equilibrium statistical mechanics cannot be used. Despite the lack of a general theory, much progress has been made in the study of surface reaction models. These models have been extensively studied through the use of Monte-Carlo simulations, reaction-diffusion equations, and mean-field rate equations. In this work, variations of the AB$_2$ model were analyzed to determine the phase diagram, critical points, reaction kinetics, and interface propagation. A theory for chemical diffusion in mixed adlayers was developed and successfully applied to both the AB$_2$ model and the NO+CO model.

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