

Kinetic phase transitions in a surface-reaction model: Mean-field theory

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A kinetic model for irreversible surface reactions, recently proposed by Ziff, Gulari, and Barshad, is studied in the site and pair approximations. The latter approach predicts the phase diagram correctly, and yields quantitative predictions which are in very close agreement with simulation, in the vicinity of the first-order kinetic transition.

Kinetic or nonequilibrium phase transitions^{1,2} are of growing interest in physical and biological sciences. There has been considerable progress toward understanding such phenomena, but a general theory has yet to be developed, and so studies of simple models can be quite illuminating. Many of the models proposed in this context are of a mean-field character, in that the quantities of interest are average densities. A kinetic model recently proposed by Ziff *et al.*³ is of particular interest in this regard, since spatial inhomogeneities are not averaged out, and long-range correlations may in principle be generated in the course of the evolution. If long-range correlations play an important role in the dynamics, one would not expect mean-field theory to describe the phase diagram accurately. In this paper we will show that the kinetic phase transitions observed in simulations of this model³ may in fact be understood on the basis of a mean-field approach. After a brief review of the model (a more complete discussion will be found in Ref. 3), equations of motion in the site and pair approximations are derived, and the resulting predictions for the phase diagram are examined.

The model introduced by Ziff and co-workers describes certain aspects of the reaction $\text{CO(ads)} + \text{O(ads)} \rightarrow \text{CO}_2$, where the qualifier "ads" denotes a species adsorbed onto the surface of a catalyst. The catalyst is modeled as a square lattice; each site may be empty or occupied by an oxygen (O) atom or a carbon monoxide (CO) molecule. CO molecules arrive at the surface at a rate y_{CO} and, upon encountering a vacant site, immediately adsorb. O₂ molecules arrive at the rate $y_{\text{O}} = 1 - y_{\text{CO}}$ and adsorb if they encounter a nearest-neighbor pair of vacant sites. (Molecules incident upon occupied sites are reflected from the surface.) Once a molecule settles on the lattice, it remains fixed: Surface diffusion and desorption are ignored in this model, which is therefore intrinsically irreversible. The only dynamic process occurring on the lattice is the oxidation of CO. When a CO molecule adsorbs, if any of its four nearest neighbors is occupied by an O atom, the CO and O react to form CO₂. Upon adsorption of an O₂, the molecule dissociates so that the two O atoms are free to react independently. If either O atom finds itself adjacent to a CO, a CO₂ molecule is again formed. CO₂ molecules are assumed to leave the lattice immediately, so that production of CO₂ opens up sites for possible absorption. A fully occupied lattice is said to be "poisoned," since no further evolution is possible.

Ziff and co-workers observed three steady-state regimes or phases in the model: for $0 < y_{\text{CO}} \leq y_1$, and O-poisoned phase; for $y_1 < y_{\text{CO}} < y_2$, a reactive steady state in which CO₂ is continuously produced; and for $y_{\text{CO}} \geq y_2$, a CO-poisoned phase. The transition from the O-poisoned phase to the reactive phase is continuous, or second order, while the transition from the reactive to the CO-poisoned phase is first order.

Site approximation. In order to analyze the kinetics of the surface reaction model, it is useful to distinguish the following five processes:

- (1) O₂↓,
- (2) O₂↓, CO₂↑,
- (3) O₂↓, 2CO₂↑,
- (4) CO↓,
- (5) CO↓, CO₂↑.

(Occurrences of process k will be referred to as " k events.") In a 1-event, for example, and O₂ molecule adsorbs at a pair of nearest-neighbor vacant sites, with both O atoms remaining on the surface, there being no CO molecules at any of the six neighboring sites. Let N_{O} and N_{CO} denote, respectively, the numbers of sites occupied by O and by CO, let $N_{\text{B}} = N - N_{\text{O}} - N_{\text{CO}}$ denote the number of vacant sites (in a lattice with a total of N sites), and let $x_i \equiv N_i/N$ denote the corresponding concentrations. In the site approximation we estimate the rates of processes 1–5 on the basis of the x_i , ignoring all spatial correlations. Thus the probability of finding a nearest-neighbor pair of vacant sites is taken to be x_{B}^2 . Approximating the rates of processes 1–5 in this manner, one readily derives the following equations of motion for the concentrations

$$\frac{dx_{\text{O}}}{dt} = 2y_{\text{O}}x_{\text{B}}^2(1-x_{\text{CO}})^3 - y_{\text{CO}}x_{\text{B}}[1-(1-x_{\text{O}})^4], \quad (1)$$

$$\frac{dx_{\text{C}}}{dt} = -2y_{\text{O}}x_{\text{B}}^2[1-(1-x_{\text{CO}})^3] + y_{\text{CO}}x_{\text{B}}(1-x_{\text{O}})^4, \quad (2)$$

where $x_{\text{B}} = 1 - x_{\text{O}} - x_{\text{CO}}$ and $y_{\text{O}} = 1 - y_{\text{CO}}$. Subtraction yields

$$\frac{d(x_{\text{O}} - x_{\text{CO}})}{dt} = 2y_{\text{O}}x_{\text{B}}^2 - y_{\text{CO}}x_{\text{B}} \quad (3)$$

so that in the steady state either $x_{\text{B}} = 0$ (poisoned surface) or

$$\bar{x}_B = \frac{y_{CO}}{2(1-y_{CO})} = Y. \quad (4)$$

(We shall denote steady-state values by overbars.) Inserting Eq. (4) into Eq. (2), one finds that in the reactive steady state \bar{x}_{CO} satisfies

$$(Y + \bar{x}_{CO})^4 + (1 - \bar{x}_{CO})^3 - 1 = 0. \quad (5)$$

For small values of Y there are two solutions, $\bar{x}_<$ and $\bar{x}_>$ ($\bar{x}_< < \bar{x}_>$), in the interval $[0,1]$, which coalesce when $Y = 0.638986$, corresponding to $y_{CO} = y_s = 0.561013$, and $\bar{x}_{CO} = 0.166011$. The reactive steady state exists only for $y_{CO} < y_s$, and so y_s marks a spinodal point. Numerical integration of Eqs. (1) and (2) reveals that for $y_{CO} < y_s$, starting from an empty lattice, the system attains a reactive steady state, with $\bar{x}_{CO} = \bar{x}_<$. For $y_{CO} > y_s$ the final state is poisoned, with almost all sites occupied by CO. (About 0.2% of the sites are occupied by O atoms in this state.) The values $\bar{x}_B = Y$, $\bar{x}_{CO} = \bar{x}_>$ comprise an *unstable* steady state: Starting from $x_B = Y$ and $x_{CO} = \bar{x}_> + \epsilon$ (with ϵ a small positive number), the poisoned state is reached; the initial condition $x_B = Y$, $x_{CO} = \bar{x}_> - \epsilon$ evolves to the reactive steady state.

While the reactive phase remains viable up to $y_{CO} = y_s$, we may expect it to become progressively less stable as the spinodal is approached. One expects that for some $y_2 \leq y_s$, there is a first-order phase transition in the sense that the poisoned state is more stable than the reactive one. In contrast to the situation in equilibrium thermodynamics, the relative stability of phases cannot here be determined from a free energy. We adopt instead the inherently kinetic criterion proposed by Ziff *et al.*³ They determined the phase boundary by considering the evolution from an initial state in which half of the lattice is completely covered by CO, and the other half is vacant. The phase boundary y_2 is defined such that for $y_{CO} < y_2$, this initial condition evolves to a reactive steady state, while for $y_{CO} \geq y_2$ the system poisons with CO. The simulations reveal a first-order transition at $y_{CO} = y_2 = 0.525 \pm 0.001$. In an analogous manner, we locate the phase boundary $y_2^{(s)}$ by determining whether Eqs. (1) and (2) attain a reactive or a poisoned steady state, when initially $x_{CO} = x_B = \frac{1}{2}$. This yields a first-order transition at $y_2^{(s)} = 0.4787$, about 9% below the simulation value. (Note, however, that the site approximation does not distinguish between the segregated initial conditions employed in the simulations and an homogeneous mixture of vacant and occupied sites, so that the initial conditions for theory and simulation are not precisely equivalent.)

The key qualitative failure of the site approximation is its prediction of a reactive steady state for all y_{CO} in the range $(0, y_2^{(s)})$. In the simulations the reactive steady state is observed only for $y_1 < y_{CO} < y_2$, with $y_1 = 0.389 \pm 0.005$; for $y_{CO} < y_1$, an initially empty lattice evolves to an O-poisoned state. y_1 marks a *second-order* kinetic phase transition: \bar{x}_c and the rate \bar{R} of CO₂ production increase continuously from zero as y_{CO} is increased above y_1 . In the site approximation, O-CO nearest-neighbor pairs (forbidden in the model), are in effect tolerated, due to the neglect of spatial correlations. This leads to an overestimate of the stability of CO-bearing phases, so that the

second-order transition observed in simulation is absent, and the transition to the CO-poisoned phase is predicted to occur at a smaller y_{CO} value than is observed in simulation. The insensitivity of the site approximation to the composition of nearest-neighbor pairs is also responsible for the small fraction of remnant O sites in the CO-poisoned phase: True poisoned states obviously consist of a unique species.

Pair approximation. Since the shortcomings of the site approximation appear to be due largely to neglect of the prohibition against O-CO nearest-neighbor pairs, it is natural to examine the pair approximation, which is the next in a series of progressively more accurate (and more complicated) cluster methods. There are five allowed nearest-neighbor or bond types, so that at this level of description the evolution is governed by a set of four coupled equations for the bond concentrations.

Derivation of the equations of motion proceeds in a manner similar to that used in the site approximation, but is now somewhat more complicated. Consider, for example, process 1. The rate at which O₂ molecules adsorb on the lattice is $y_O x_{BB}$, where x_{ij} ($i, j = B, CO, \text{ or } O$), denotes the concentration of i - j bonds. Using simple combinatorial arguments familiar from polymer lattice statistics,⁴ one finds that the probability for a site to be of type i , given that one of its nearest neighbors is of type j , is

$$P(i | j) = \frac{x_{ij}}{2x_j}, \quad (6)$$

where $x_j = \frac{1}{2}(x_{jj} + \sum_i x_{ij})$ again denotes the concentration of j sites. Thus, in the pair approximation we estimate the rate of process 1 as

$$y_O x_{BB} (1 - x_{BCO} / 2x_B)^6.$$

In each 1-event, N_{BB} (the number of B - B bonds) is reduced by at least 1, since a pair of empty sites are occupied by O's. If any of the six nearest neighbors of the B - B pair also happen to be empty, additional B - B bonds are lost. In process 1 the neighbors of the central B - B pair may not be occupied by CO molecules (or else the O atoms would react), so that in this case the probability that a given neighbor is empty is

$$P(i = B | j = B, i \neq CO) = \frac{2x_{BB}}{2x_{BB} + x_{BO}}. \quad (7)$$

The average change in the number of B - B pairs attending a 1-event may therefore be approximated as

$$\Delta N_{BB}^{(1)} = -1 - \frac{12x_{BB}}{2x_{BB} + x_{BO}}. \quad (8)$$

[Note that Eqs. (6) and (7), which refer only to pair probabilities, are exact, whereas in writing Eq. (8) we ignore three-body and higher-order correlations.]

Proceeding in this fashion, one may derive the rates and bond-number changes for each process. For processes 2 and 3 it proves useful to distinguish between two sub-processes, characterized by different ΔN_{ij} values. Process 2a refers to the case in which the reacting CO lies off the line joining the sites where O₂ adsorbs, while in 2b the

TABLE I. Rates and changes in bond number in the pair approximation.

Process	Rate	ΔN_{BB}	ΔN_{BO}	ΔN_{BCO}	ΔN_{OO}
1	$y_O x_{BB} (1-u)^6$	$-1 - 12\alpha x_{BB}$	$6\alpha(2x_{BB} - x_{BO})$	0	$1 + 6\alpha x_{BO}$
2a	$4y_O x_{BB} u (1-u)^3 \left[1 - u + \frac{u^2}{3}\right]$	$\frac{x_{BCO}}{x_{CO}} - 4\alpha x_{BB}$	$8\alpha x_{BB}$	$-2 \frac{x_{BCO}}{x_{CO}}$	$2\alpha x_{BO}$
2b	$\frac{1}{2} R^{(2a)}$	$\frac{3x_{BCO}}{2x_{CO}} - 6\alpha x_{BB}$	$2\alpha(4x_{BB} - x_{BO})$	$2 \frac{x_{CO} x_{CO} - x_{BCO}}{x_{CO}}$	$3\alpha x_{BO}$
3a	$y_O x_{BB} u^2 (2 - 4u + \frac{10}{3}u^2 - \frac{4}{3}u^3 + \frac{2}{9}u^4)$	$3 + 2 \frac{x_{BCO}}{x_{CO}}$	0	$2 \frac{x_{CO} x_{CO} - 3x_{BCO}}{x_{CO}}$	0
3b	$\frac{7}{2} R^{(3a)}$	$2 + 3 \frac{x_{BCO}}{x_{CO}}$	0	$4 \frac{x_{CO} x_{CO} - x_{BCO}}{x_{CO}}$	0
4	$y_{CO} x_B (1-v)^4$	$-12\beta x_{BB}$	0	$4\beta(2x_{BB} - x_{BCO})$	0
5	$y_{CO} x_B [1 - (1-v)^4]$	$1 + 3 \frac{x_{BO}}{x_O}$	$2 \frac{x_{OO} - x_{BO}}{x_O}$	0	$-3 \frac{x_{OO}}{x_O}$

where

$$u = x_{BCO}/2x_B$$

$$v = x_{BO}/2x_B$$

$$\alpha = (2x_{BB} + x_{BO})^{-1}$$

$$\beta = (2x_{BB} + x_{BCO})^{-1}$$

reacting CO lies on this line; in 3a the reacting CO's are nearest neighbors, while in 3b they are not (see Fig. 1). To find the rates for processes 2a, 2b, 3a, and 3b, one partitions the set of all relevant configurations of the B - B pair and its six nearest neighbors into disjoint subsets, and determines, for each subset, the probability of occurrence and the branching rate for the a and b subprocesses. As an example, consider the arrangements depicted in Fig. 2. Configurations of type I (in which the only CO lies off the line joining the B - B pair), occur (in the pair approximation) with probability $4u(1-u)^5$ ($u = x_{BCO}/2x_B$), and always result in a 2a-event when an O_2 is adsorbed at the central B - B pair. Configurations of type II occur with probability $2u^3(1-u)^3$, and result in 2a-events with probability $\frac{2}{3}$, and in 2b-events with probability $\frac{1}{3}$. (Three additional configuration types must be considered in deriving the rates for processes 2a and 2b.) In the pair approximation the equations of motion are

$$\frac{dx_{ij}}{dt} = \sum_k R^{(k)} \Delta N_{ij}^{(k)}. \quad (9)$$

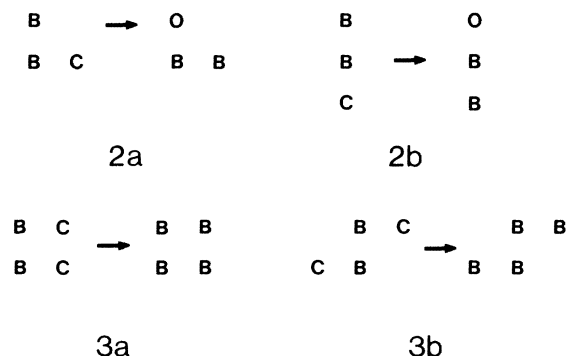
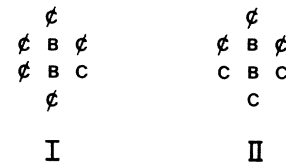


FIG. 1. Examples of processes 2a, 2b, 3a, and 3b, which are distinguished in the pair approximation.

The rates $R^{(k)}$ and bond-number changes $\Delta N_{ij}^{(k)}$ are listed in Table I.

We now examine the phase diagram in the pair approximation, as determined via numerical integration of the equations of motion. Consider first the steady states evolving from an initially empty lattice. For $0 < y_{CO} \leq y_1^{(p)} = 0.2497$, the lattice poisons with oxygen, and as y_{CO} is increased above $y_1^{(p)}$, \bar{x}_{CO} and \bar{R} are found to increase continuously from zero. Thus the pair approximation correctly predicts a second-order transition from the O-poisoned state to the reactive state, albeit at a substantially smaller y_{CO} value than is observed in simulations (cf. 0.389 ± 0.005). For $y_1^{(p)} \leq y_{CO} \leq y_s = 0.561013$, a reactive steady state is attained, while for $y_{CO} > y_s$ the system poisons with CO. The pair approximation therefore yields the same value for the spinodal, y_s , as does the site approximation.

To locate the phase boundary $y_2^{(p)}$, we again examine the asymptotic behavior resulting from the initial state of a lattice half filled with CO and half empty. The initial values $x_{BB} = x_{CO} = \frac{1}{2}$ (with the other bond concentrations initially zero), faithfully represent the initial condi-

FIG. 2. Examples of configuration types relevant to the evaluation of the rates for processes 2a and 2b in the pair approximation. "C" denotes a site which may not be occupied by CO, but is otherwise unspecified. When O_2 molecule adsorbs at the B - B pair, configuration I always results in a 2a-event. Configuration II yields a 2a-event with probability $\frac{2}{3}$, and a 2b-event with probability $\frac{1}{3}$.

tions employed in the simulations. One finds a first-order transition at $y_2^{(p)} = 0.52410$, in agreement with the simulation value of 0.525 ± 0.001 . A comparison of the pair-approximation predictions and simulation results is presented in Fig. 3. Evidently, this level of approximation yields very accurate predictions in the vicinity of the first-order transition. The accuracy of mean-field theory in this region may be attributed to the shortness of the correlation length, as reflected in the small size of the CO clusters observed in simulations of the reactive steady state.³ The divergence between theory and simulation at lower y_{CO} values presumably indicates the importance of longer-ranged correlations near the second-order transition. But the mean-field approach employed here does predict the qualitative nature of the transition correctly: At the second-order transition, \bar{x}_{CO} and \bar{R} increase linearly with y_{CO} in theory and in simulation. There is evidence of slowing down at the second-order transition: The time required to attain the steady-state scales, in the pair approximation, as $|y_{CO} - y_2^{(p)}|^{-1}$ near $y_2^{(p)}$.

The relaxation time also becomes large in the vicinity of the spinodal. An example of interesting time-dependent behavior near the spinodal is shown in Fig. 4, which depicts the site concentrations predicted by Eq. (9), starting from an initially empty lattice. Here $y_{CO} = 0.5611$, just above the spinodal. In the early stage of the evolution, O₂ and CO rapidly adsorb, and attain quasisteady concentrations within a few time units. Over the next 250 time units O is gradually displaced by CO, while x_B remains virtually constant, until a critical value is reached and the surface rapidly poisons. This sequence of events is a nonequilibrium analog of the familiar nucleation "bottleneck" phenomenon. The pair-approximation equations of motion may prove useful in understanding variations

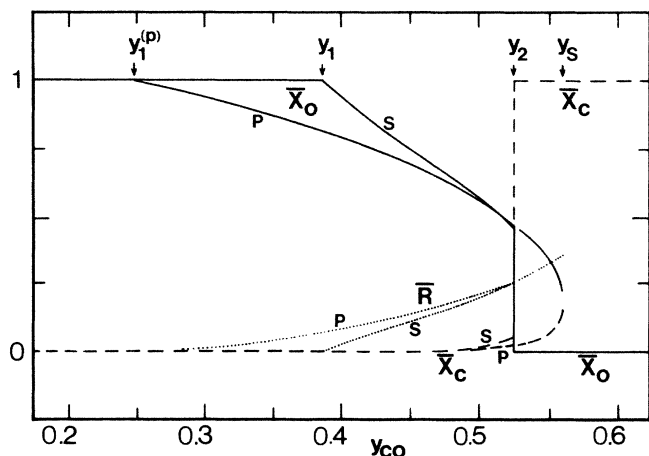


FIG. 3. Comparison of the theoretically predicted phase diagram (pair approximation) with simulation results. Solid line: \bar{x}_O , the fraction of sites occupied by O atoms in the steady state; dashed line: \bar{x}_{CO} , the occupation fraction for CO; dotted line: \bar{R} , the rate of CO₂ production. Curves labeled "P" represent pair-approximation predictions; "S" denotes simulation results. Curves to the right of the phase transition at y_2 depict the metastable reactive steady state, as given in the pair approximation.

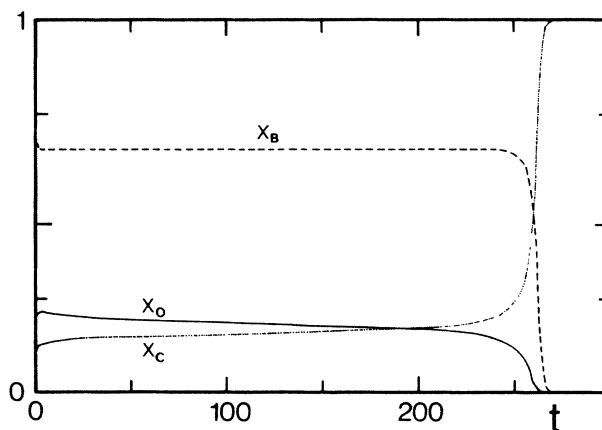


FIG. 4. Solution of the pair-approximation equations of motion, starting from an initially empty lattice, with $y_{CO} = 0.5611$, just above the spinodal value.

ous dynamical aspects (e.g., transient effects, periodic operation) of the catalytic process.

The behavior at the point $y_{CO} = 0$ deserves special comment. In this case each O₂ molecule which adsorbs remains fixed on the lattice, so the model corresponds to the random dimer filling problem.⁵ A certain fraction of sites remain vacant in the final state, since the O₂ molecules may adsorb only at vacant pairs. The pair approximation predicts a maximum occupancy in random dimer filling of 0.8885, as compared with the best estimate⁵ of 0.907. We have also examined the predictions of the pair approximation for a one-dimensional chain. In this case the phase diagram is rather uninteresting, since the lattice is always poisoned by O or CO. The pair approximation does, however, predict a maximum occupancy of $1 - e^{-2} = 0.864664 \dots$ for one-dimensional random dimer filling, reproducing the exact value derived long ago by Flory.⁶

The mean-field approach, at the pair-approximation level, has been shown to predict the properties of the surface reaction model quite accurately, particularly in the vicinity of the first-order transition. The shortcomings of the theory in regards to the second-order transition may perhaps be ameliorated by considering large clusters. While more complicated than the methods applied here, such studies would not be impractical, as there are only 12 squares, and also 12 triplets, admissible in the model. However, the qualitative nature of the transitions is already clear: The concurrence of simulation and the present theory implies that they are of the mean-field type. Kinetic phase transitions in nonequilibrium lattice-gas models^{7,8} are also known to be of a mean-field nature.

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