

Symmetry-Breaking and Percolation Transitions in a Surface Reaction Model with Superlattice Ordering

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(Received 12 August 1999)

A symmetry-breaking order-disorder transition of the Ising type is found in a *nonequilibrium* surface reaction model for CO oxidation incorporating superlattice ordering of adsorbed oxygen. We relate this transition to the percolation of superlattice domains of oxygen, and discuss the consequences for chemical diffusion of coadsorbed CO. The latter constitutes a new type of problem involving transport in disordered media.

PACS numbers: 82.65.Jv, 64.60.Ak, 64.60.Cn, 68.35.Rh

Much of the impetus for studying chemisorption systems has derived from the more challenging goal of understanding and controlling catalytic surface reactions. There has been considerable effort and success in using surface-sensitive probes to characterize spatial ordering or self-organization in nonreactive chemisorbed adlayers on single-crystal substrates [1]. Furthermore, it is well recognized experimentally that such ordering of the adlayer persists during surface reaction [2], and that it can even be modified by the adsorption and reaction processes. In fact, the influence of islanding of reactants on the reaction kinetics was explored in early studies, although mainly with heuristic modeling [3]. Recent studies of surface reactions have also examined the rich variety of mesoscale spatial pattern formation exhibited by these reaction-diffusion systems [4]. However, there has been little consideration of the effect of ordering in reactant adlayers on diffusion and pattern formation.

Atomistic lattice-gas models have been applied to provide a sophisticated description of spatial ordering and phase transitions in nonreactive equilibrated adlayers, and to extract information on adspecies interactions from the observed ordering [1]. The same approach can potentially be applied to describe reactive systems. However, most such modeling of surface reactions has not incorporated key aspects of the process, such as high surface mobility of some reactant species, e.g., CO in CO oxidation [5], adspecies interactions, and “ensemble requirements” of the adsorption process [6,7]. As a result, the steady-state behavior [8] has exhibited non-physical features (e.g., large fluctuations and negligible hysteresis due to neglect of mobility, and continuous poisoning transitions due to idealized interactions and adsorption rules). Here we shall see that more realistic models exhibit ordering and percolation behavior which is in some respects analogous to, but also somewhat different from, “corresponding” equilibrium behavior.

Specifically, in this Letter, we focus on the effect of incorporating strong short-range repulsive adspecies interactions into reaction models. Such interactions

are present in many chemisorption systems, and produce superlattice ordering of the adlayer (with a unit cell larger than that of the substrate). We show that these interactions induce spontaneous symmetry-breaking transitions in the nonequilibrium steady state of the adlayer. These transitions, which could be observed with LEED, are a direct analog of order-disorder transitions in equilibrated adlayers [1], for which an ongoing theoretical challenge is to provide a geometric interpretation [9]. We also take up this issue for the reaction model, exploring the relationship between the symmetry-breaking transition and the percolative properties of the superlattice domains in the adlayer. Results even shed light on behavior for equilibrated adlayers, which constitutes a limiting case of the reaction model. The motivation for characterizing adlayer structure in reaction models is that this influences the chemical diffusion of coadsorbed species (in this case, percolative diffusion along domain boundaries), which in turn controls spatiotemporal behavior. Thus, we also analyze key features of this novel transport problem.

We explore these issues using a lattice-gas model for catalytic CO oxidation on a square lattice of adsorption sites. This model incorporates the appropriate Langmuir-Hinshelwood mechanism, very rapid mobility of adsorbed (ads) CO, and infinite nearest-neighbor (NN) repulsions between adsorbed oxygen resulting in checkerboard or $c(2 \times 2)$ ordering (see Fig. 1). Specifically, the model includes the following steps.

(i) CO(gas) adsorbs onto single empty sites at rate p_{CO} . CO(ads) hops very rapidly to other empty sites on the surface. There are no interactions between CO(ads) and other CO(ads) or O(ads), except site exclusion, so the “infinitely mobile” CO(ads) is assumed to be randomly distributed on sites not occupied by O(ads).

(ii) O₂(gas) adsorbs dissociatively at diagonal or second NN empty sites at rate p_{O_2} , provided that the additional six sites adjacent to these are not occupied by O(ads). This “eight-site rule” reflects the very strong NN O(ads)-O(ads) repulsions [10].

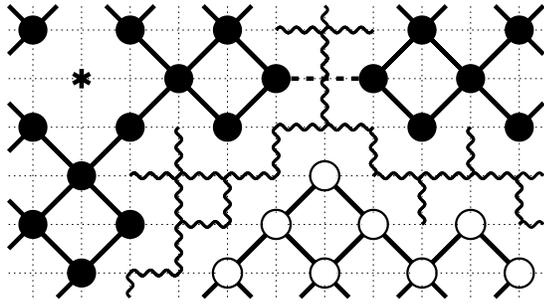


FIG. 1. $c(2 \times 2)$ domain structure. Empty and filled circles denote O(ads) on different $c(2 \times 2)$ sublattices. Solid bonds denote second NN domains. The two second NN domains at the top form a single third NN domain. A NN vacancy domain dual to the second NN $c(2 \times 2)$ domains, which also corresponds to a domain boundary, is shown by the wiggly bonds. “*” denotes an “isolated defect”.

(iii) O(ads) hops to NN empty sites with rate h_O , provided that this process does not create any NN O(ads)-O(ads) pairs.

(iv) Each adjacent pair of CO(ads) and O(ads) reacts at rate k to form CO_2 which immediately desorbs.

One feature of this model is bistability: a stable “reactive” state with high O coverage, θ_O , and low CO coverage, θ_{CO} , coexists with a stable “inactive” state with $\theta_{\text{CO}} = 1$ [6]. In this paper, we focus on the behavior of the reactive steady-state. We note that our model is a variant of those considered recently in Refs. [6,7]. In contrast, most of the previous work was based on the Ziff-Gulari-Barshad model [11] and refinements with rapid CO mobility [5], which assumed oxygen adsorption on adjacent sites, and neglected adspecies interactions. This resulted in an artificial oxygen poisoning transition, which is absent in our model.

In this paper, we consider only the regime of large reaction rate k (as in Ref. [7]). Together with the infinite mobility of CO(ads), this implies that θ_{CO} is negligible in the reactive steady state. We thus naturally map the model onto a simpler single-species problem involving adsorption of $\text{O}_2(\text{gas})$ dimers, and desorption (and hopping) of O(ads) monomers. Dimer adsorption obeys the eight-site rule with attempt rate p_{O_2} . To determine the monomer desorption rate, d_O , note that the adsorption rate per site of CO is $p_{\text{CO}}(1 - \theta_O)$. In a steady state, this must be balanced by the desorption rate per site for oxygen of $d_O\theta_O$, so $d_O = p_{\text{CO}}(1 - \theta_O)/\theta_O$. Thus we are left with only three adjustable parameters, p_{O_2} , d_O , and h_O , and typically present results in terms of the reduced oxygen adsorption rate $u_O = p_{\text{O}_2}/(p_{\text{O}_2} + d_O)$. Henceforth, we mostly drop the subscripts.

We now provide a brief overview of steady-state behavior, and its dependence on oxygen mobility. Note that oxygen is relatively immobile so that the case $h = 0$ is of particular interest. However it is instructive to contrast behavior with the limit $h \rightarrow \infty$ which corresponds to the equilibrium hard square (HS) model [12–14]. Figure 2 shows

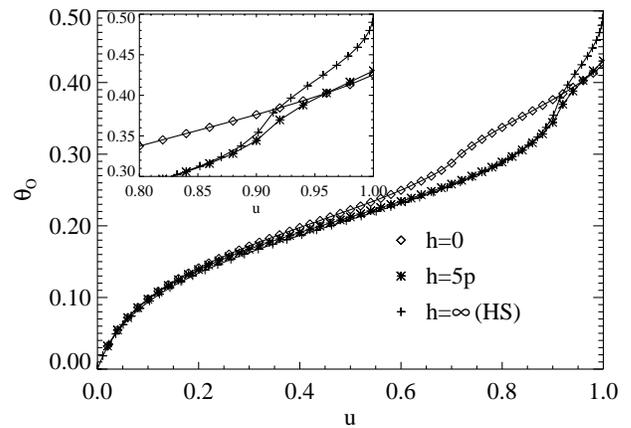


FIG. 2. Dependence of the O(ads) coverage on the reduced $\text{O}_2(\text{gas})$ -dimer deposition rate $u = p/(p + d)$, for O(ads) diffusion rates $h = 0$ and $h = 5p$. Also plotted is the result for the hard square model, which corresponds to the $h \rightarrow \infty$ limit.

the dependence of steady-state O(ads) coverage, θ_O , on u , for $h = 0, 5p$, and ∞ . For lower θ_O , oxygen mobility with $h = 5p$ is sufficient to effectively equilibrate the adlayer. However, for higher θ_O , the diffusion dynamics through NN hopping is highly constrained [14], producing behavior more like $h = 0$. We now comment further on behavior in the limit $u \rightarrow 1$ (high oxygen adsorption rates). For $h = \infty$ (the HS model), $\theta_O \rightarrow 0.5$, the maximum allowable value. For $h = 0$, however, $\theta_O(u \rightarrow 1) \approx 0.4253$ is lower, since slow removal of oxygen by reaction produces “isolated defects” within $c(2 \times 2)$ domains which cannot be immediately filled by oxygen dimer adsorption. As h increases, $\theta_O(u \rightarrow 1)$ increases, although very slowly, e.g., $\theta_O(u \rightarrow 1, h/p = 128) = 0.4336$.

It is well known that the HS model (corresponding to the reaction model with $h = \infty$) undergoes a symmetry-breaking phase transition at $\theta_O = 0.367743$ [12] (and $u_c \approx 0.909$). Above this critical coverage, the particles exhibit long-range $c(2 \times 2)$ ordering, i.e., an imbalance develops in the coverages, θ_{\pm} , of the two $c(2 \times 2)$ sublattices shown in Fig. 1. This transition is believed to be second order within the Ising universality class [12].

To study the critical behavior of the reaction model for $h < \infty$, we employ finite size scaling on $L \times L$ lattices with periodic boundary conditions. The transition point is located using a fourth order cumulant of the order parameter $Q_L = \langle m^4 \rangle / \langle m^2 \rangle^2$, where $m = \theta_+ - \theta_-$ is the order parameter and $\langle \dots \rangle$ denotes the ensemble average. Figure 3(a) shows Q_L as a function of u in the reaction model with $h = 0$. As in equilibrium models undergoing continuous phase transitions, curves for different L tend to cross at the same point as L approaches infinity. We estimate $u_c = 0.7135(5)$ and $\theta_c = 0.2964(6)$. To obtain the critical exponents, we use the following finite size scaling form for some physical quantity P in an $L \times L$ system:

$$P_L \sim L^{\chi/\nu} F[(u - u_c)L^{1/\nu}], \quad (1)$$

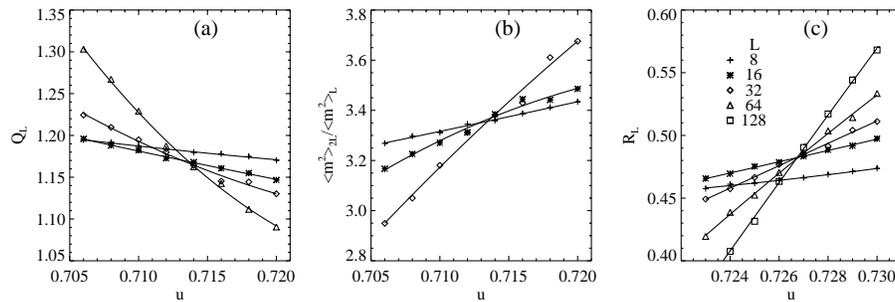


FIG. 3. Finite size scaling (FSS) for the reaction model in the case $h = 0$. (a) $Q_L(u) = \langle m^4 \rangle_L / \langle m^2 \rangle_L^2$; (b) $\langle m^2 \rangle_{2L} / \langle m^2 \rangle_L$, and (c) the spanning probability R_L for second NN connectivity. Each data point is obtained through an average over 4×10^6 Mc steps.

where χ and ν are the critical exponents for P and the characteristic length, and $F(y) \sim y^\chi$, as $y \rightarrow \infty$. One can determine both u_c and χ/ν by plotting P_{2L}/P_L for different L 's. As an example, Fig. 3(b) shows such scaling for the fluctuations of the order parameter $\langle m^2 \rangle$ for $h = 0$. Using systems of $L = 8$ to 64 , we estimate $\gamma/\nu = 1.748(5)$ and separately $\nu = 0.98(2)$, consistent with the values $7/4$ and 1 , respectively, for the 2D Ising universality class.

Theoretical efforts to provide a geometric interpretation for phase transitions in equilibrium systems were noted above [9]. Along these lines, for the reaction model, we first explore the relationship between the symmetry-breaking transition and the percolative properties of $c(2 \times 2)$ -O(ads) domains with second NN connectivity (see Fig. 1). The motivation comes from consideration of diffusion of coadsorbed CO in the reaction model. If the dominant CO-diffusion mechanism is through hopping between NN sites unoccupied by O(ads), then the chemical diffusion coefficient vanishes at the second NN percolation point. This follows since second NN connectivity of $c(2 \times 2)$ -O(ads) domains is dual to NN connectivity of the unoccupied domains on which CO can diffuse (see Fig. 1).

Since percolation of a (second or third NN) $c(2 \times 2)$ domain of one phase would block percolation of domains of the other phase, by symmetry neither phase can percolate below the symmetry-breaking transition [15]. Thus percolation could only occur either (A) at the phase transition or (B) above the phase transition. In scenario B, since the correlation length is finite, percolation should belong to the random percolation universality class. In scenario A, a divergent correlation length can change the percolation to a different universality class.

For the reaction model with $h = 0$, we find that scenario B occurs, i.e., there is a finite gap between the percolation transition for the second NN connectivity and the symmetry-breaking transition. Figure 3(c) plots the probability $R_L(u)$ that an $L \times L$ system percolates. As $L \rightarrow \infty$, $R_L(u)$ approaches a step function and finite size scaling predicts that $R_L(u)$ for different L should cross at the percolation point. Figure 3(c) clearly shows that the percolation point is *different* from the ordering transition point.

We estimate the $u_p^{2NN} = 0.727(1)$ and $\theta_p^{2NN} = 0.3052(6)$ for $h = 0$. As expected, critical exponents determined from finite size scaling are consistent with the random percolation values.

For the hard square model (i.e., the reaction model with $h = \infty$), previous simulations suggested the coincidence of percolation and phase transition points [16]. Our more extensive simulations [13] are consistent with this claim. Figure 4 shows the finite size scaling result for the average second NN cluster size $s_{av} = \sum s^2 n_s / \sum s n_s$, where n_s is the number of clusters of size s . We can determine both the percolation point (for comparison with the ordering transition) and the critical exponent from the intersecting point of the curves.

One consequence of the percolation transition coinciding with a second order phase transition in the HS model is that the universality class can be moved away from that of classical random percolation. Table I lists some critical exponents for percolation obtained from finite size scaling. The values quoted are normalized by the characteristic length exponent ν . The value of ν is rather difficult to determine using Monte Carlo (MC) methods, but is consistent with the Ising value, i.e., $\nu = 1$. Here d_f is the fractal dimension, and γ_p is the exponent for the average cluster size. We also consider percolation of $c(2 \times 2)$ domains with third NN connectivity (see Fig. 1), where the coincidence with the phase transition is established [9]. These

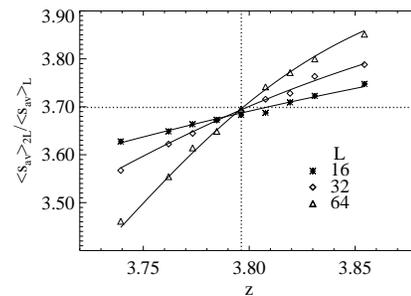


FIG. 4. FSS of the average cluster size s_{av} for the second NN connectivity in the HS model. The vertical dotted line indicates the critical activity $z_c = 3.79626$ for the ordering transition [13]. The corresponding y value is $2^{y_p/\nu}$.

TABLE I. FSS results for the HS model. Values obtained are consistent with the scaling relation $\tilde{\gamma}_p \equiv 2(d_f - 1)$.

d_f (2NN)	$\tilde{\gamma}_p$ (2NN)	d_f (3NN)	$\tilde{\gamma}_p$ (3NN)	d_f (vac)	$\tilde{\gamma}_p$ (vac)
1.947(1)	1.895(2)	1.948(2)	1.897(2)	1.390(6)	0.80(1)

exponent values differ significantly from random percolation where $d_f = 91/48$, $\gamma_p = 43/18$, and $\nu = 4/3$. Also distinct from random percolation is the behavior of the spanning probability R_L which is central to renormalization group calculations. Numerical evidence suggests that $R_L(u_p)$ assumes a value very close to 1 rather than $1/2$ as for random percolation [17].

We also study the percolation of vacancy clusters with NN connectivity, because of the relevance to CO diffusion in the reaction model. The percolation point must coincide with that for second NN $c(2 \times 2)$ domains because of the above-mentioned duality. When $h = 0$, we find random percolation values for critical exponents, as for the second NN $c(2 \times 2)$ domains. For the HS model, we find much smaller d_f and γ_p than in all other cases (see Table I). This feature is clarified by configuration snapshots which reveal that vacancy clusters are less ramified than in the case $h = 0$. As noted above, the CO diffusion coefficient, D , vanishes at this percolation point for CO diffusion via hopping between adjacent unoccupied sites. Near the critical point, one has $D \sim (u - u_p)^\mu$. For the HS model, a numerical study using a node elimination method [18] shows that μ/ν has a larger value 1.41(3) than the random percolation value of 0.98 (applying for $h = 0$) and strongly violates the Alexander-Orbach conjecture that implies $\mu/\nu = d_f(\text{vac})/2$. Thus, this CO-diffusion problem reveals a new type of behavior for transport in disordered media [19].

There remains the basic question of how the order-disorder and percolation behavior changes as the hopping rate h for O(ads) varies from 0 to ∞ . Critical slowing down near the transition impedes MC analysis of this issue. However, numerical evidence suggests that the gap between second NN percolation and symmetry-breaking transitions vanishes at about $h = 0.1p$. Intuitively, this is plausible. As h increases, the coverage at the ordering transition becomes significantly larger than the percolation point of 0.29637 if one of the sublattices is occupied randomly. Thus for large h , one might expect percolation to occur as soon as it is possible (i.e., right at the symmetry-breaking transition). From another perspective, one might argue that a finite gap between second NN percolation point and ordering transitions seems counter to the physical intuition that long-range order can only occur when the system exhibits long-range "communication" via percolation [9]. However, one can argue that dimer deposition introduces an effective "interaction" of longer

range than NN. Therefore, in order to ensure coincidence between the symmetry-breaking and percolation transitions, we need longer-range connectivity. Indeed, we find that third NN percolation does coincide with the ordering transition point for all h including $h = 0$.

In summary, using Monte Carlo simulations, we reveal the existence of a $c(2 \times 2)$ -O(ads) order-disorder transition in a reaction model for CO oxidation, which is of second order and in the Ising universality class. We found that coincidence of this transition with percolation of second NN $c(2 \times 2)$ domains occurs only for sufficiently mobile O(ads), where adlayer structure is closer to the HS model. The relationship between these impacts the behavior of CO diffusion, which controls pattern formation.

This work was supported by the Division of Chemical Sciences, BES, of the U.S. Department of Energy (USDOE). It was performed at Ames Laboratory which is operated for the USDOE by ISU under Contract No. W-7405-Eng-82.

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