Critical phenomena in a nonequilibrium model of heterogeneous catalysis

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A simple irreversible kinetic model recently introduced by Ziff, Gulari, and Barshad [Phys. Rev. Lett. **56**, 2553 (1986)] to describe the catalysis of chemical reactions on regular surfaces has been shown to have a second-order phase transition from an absorbing state, wherein the surface is passivated (rendered catalytically inactive or "poisoned") by one of the chemical constituents, to an active steady state. We argue here that this transition belongs in the universality class of Reggeon field theory, i.e., of directed percolation.

In a recent article, Ziff, Gularí, and Barshad[1] introduced a simple kinetic model to describe the surface catalysis of the chemical reaction $CO + O \rightarrow CO_2$. In this model, a gas composed of CO and O_2 molecules with fixed molecular concentrations of y and $1 - y$, respectively, is brought in contact with a surface, modeled as an infinite, regular (e.g., square), two-dimensional (2D) lattice. At any given time, a lattice site can be either vacant, occupied by a CO molecule, or occupied by an O atom. The rules for the adsorption and reaction of the gas molecules are as follows: (i) A CO molecule will fill any vacant site with probability γy per unit time. Here γ is an arbitrary rate constant. (ii) O_2 molecules cannot fill single vacant sites surrounded by occupied neighbors, but will, with probability $\gamma(1 - y)$ per unit time, dissociate and fill each site of any near-neighbor *pair* of vacancies with an O atom. (iii) A CO molecule and an O atom which find themselves occupying near-neighbor sites combine immediately, producing a molecule of CO_2 gas which leaves the surface and is removed from the system. Thus no two neighboring sites are ever occupied by a CO-O pair.

Since the reverse reaction $CO_2 \rightarrow CO + O$ is not allowed, the system defined by the above rules cannot satisfy detailed balance for any underlying Hamiltonian. Numerical studies[1,2] have shown that for any y it achieves, in the long-time limit, a steady state characterized by fixed concentrations of surface sites which are occupied by O atoms or by CO molecules. The results are summarized in the schematic phase diagram[1] of Fig. 1: For sufficiently small y, the surface is fully occupied or passivated (rendered catalytically inactive or "poisoned") by O atoms. At a critical value y_1 of y (with $y_1 \approx 0.39$ for the square lattice), the system undergoes a continuous phase transition into an "active" state wherein the concentrations of O atoms, CO atoms, and vacancies are all between 0 and 1, the O concentration decreasing continuously from one as y increases from y_1. At a second critical value, y_2 ($> y_1$), the system undergoes a first-order phase transition into a state wherein the surface is passivated by

CO, remaining in that state for all $y_2 < y \leq 1$. The qualitative features of this phase diagram can be obtained from mean-field approximations.[3]

Though there has been a numerical calculation[2] of the critical exponents of the continuous transition out of the oxygen-passivated "absorbing" state at y_1, the universality class into which this transition falls has not yet been identified. Attempts to make this identification are part of the larger enterprise, still in its infancy, of exploring the possible universality classes of phase transitions in none-
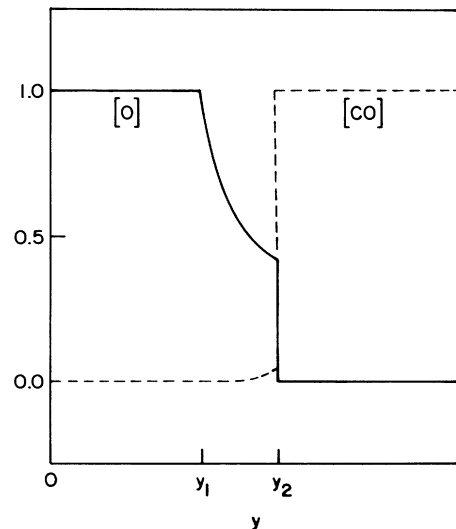

FIG. 1. Schematic phase diagram for the catalysis model described in the text. Concentrations of O (solid line) and CO (dashed line) on the surface are shown as functions of the concentration y of CO in the gas. The system undergoes (i) a continuous phase transition at $y = y_1$ from an oxygen-passivated state to an active steady state where CO_2 is produced at a fixed rate; (ii) a first-order transition at $y = y_2$ to a carbon-monoxide–passivated state.

quilibrium systems,[4] in emulation of the program which has been carried out so successfully for critical phenomena in equilibrium systems. The purpose of this note is to argue that the oxygen-passivating transition in the model catalytic reaction defined above belongs in the so-called "Reggeon field theory"[5] universality class—a class whose best-known representative is probably the directed-percolation transition.[6]

The Reggeon theory can be defined[7] by the equation of motion

$$\frac{\partial n(\mathbf{x},t)}{\partial t} = -\Gamma[-\nabla^2 n(\mathbf{x},t)$$
$$+ rn(\mathbf{x},t) + un(\mathbf{x},t)^2] + \eta(\mathbf{x},t) , \quad (1)$$

which describes the generic phase transition of a noisy system with a single-component order parameter $n(\mathbf{x},t)$ into an absorbing state[8] at $n = 0$. The correlations of the Gaussian random noise variable η satisfy

$$\langle \eta(\mathbf{x},t)\eta(\mathbf{x}',t') \rangle = \Gamma' n(\mathbf{x},t)\delta(\mathbf{x}-\mathbf{x}')\delta(t-t') . \quad (2)$$

Thus, the noise vanishes when $n = 0$, consistent with $n(\mathbf{x}, t) = 0$ being a true absorbing state from which the system cannot escape. Here Γ, Γ', r, and u are parameters, the transition out of the absorbing state occurring roughly when r first becomes negative. [This is clear in the mean-field approximation wherein the ∇^2 and noise terms in (1) are dropped, and the steady states are simply the zeros of the right-hand side: The absorbing state $n = 0$ obviously becomes unstable when r becomes negative in this case.[7]]

Though one should in principle add higher powers of n and its derivatives in (1), standard renormalization-group arguments[9] show that at least in the vicinity of the model's upper critical dimension—which is[5] four—such terms are irrelevant for determining critical properties. Thus Eq. (1) is the simplest (minimal) model of the absorbing state which possesses no symmetries other than spatial isotropy and spatial and temporal translation invariance. It is for this reason that the model describes the generic transition into an absorbing state in such a diverse group of single-component systems, chemical reactions and directed percolation being two familiar examples.[4,6,7] (This is analogous to ϕ^4 field theory describing the generic ferromagnetic transition in equilibrium Ising models.[9])

The presence of two distinct chemical components (O and CO) has thus far prevented the identification of the catalysis model defined above as a member of the Reggeon universality class.[10] To make this identification, consider a value of y just slightly above y_1, so that in equilibrium almost all of the sites are occupied by O atoms. There is some small density, n_v, of isolated vacant sites (i.e., vacant sites completely surrounded by O atoms), and of sites occupied by CO molecules. However, since each cluster of CO's must be surrounded by vacant sites, the concentration of CO's is, for y asymptotically close to y_1, small compared to the concentration of vacancies. The main effect of the CO is to produce a density, n_{vv}, of isolated near-neighbor *pairs* of vacancies, which is, even arbitrarily close to the transition, of order n_v rather than of order n_v^2. To see this, note that a CO molecule impinging on an isolated vacant site will immediately combine with

one of the surrounding oxygens, producing a vacant pair. These pairs are important in producing the absorbing (oxygen-passivated) state for $y \leq y_1$ since, unlike isolated single vacancies, they can be filled directly by O_2 molecules. For the moment then, let us consider only the two independent fields $n_v(\mathbf{x})$ and $n_{vv}(\mathbf{x})$, coarse grained in the standard manner[11] so that a field-theoretic representation becomes appropriate. Their time evolution will then be described by a set of coupled equations of the form

$$\frac{\partial n_v}{\partial t} = C_v \nabla^2 n_v + r_{11} n_v + r_{12} n_{vv} + O(n_v^2, n_{vv}^2, n_v n_{vv}) + \eta_v , \quad (3a)$$

$$\frac{\partial n_{vv}}{\partial t} = C_{vv} \nabla^2 n_{vv} + r_{21} n_v + r_{22} n_{vv} + O(n_v^2, n_{vv}^2, n_v n_{vv}) + \eta_{vv} . \quad (3b)$$

The coefficients C_v, C_{vv}, and r_{ij} are functions of the single parameter y of the microscopic model, η_v and η_{vv} are random-noise terms which account for the stochastic nature of that model, and the Laplacian terms represent the preference of the model for spatially uniform states. [For example, a higher than average density $n_{vv}(\mathbf{x})$ of vacant pairs in some region of the sample results in a higher than average rate of adsorption of O_2 molecules in that region, and hence in a reduction of $n_{vv}(\mathbf{x})$].

First, consider only the linear terms of (3), ignoring the Laplacian terms and the noise. Landau's general symmetry arguments[12] state that, in the absence of a special symmetry which ensures their vanishing, none of the r_{ij} can be zero under generic conditions. Choose the linear combinations of n_v and n_{vv}, i.e., n_+ and n_-, which diagonalize the matrix r_{ij} and hence give the linearized Eqs. (3) the form

$$\frac{\partial n_+}{\partial t} = \lambda_+ n_+ , \quad (4a)$$

$$\frac{\partial n_-}{\partial t} = \lambda_- n_- . \quad (4b)$$

The existence of the absorbing state for $y < y_1$ implies that the two eigenvalues λ_+ and λ_- are both negative for all $y < y_c^{(0)}$. [Here $y_c^{(0)}$, the mean-field critical value of y, is slightly smaller than the true critical value y_1, and would be equal to y_1 were there no nonlinear terms in Eqs. (3).] At $y_c^{(0)}$ one of the eigenvalues, such as λ_+, becomes positive, precursive to the transition out of the absorbing state at y_1. The crucial point is that, barring some accidental degeneracy, λ_- *remains negative* as λ_+ changes sign. Under generic conditions, therefore, fluctuations in the field n_- continue to decay exponentially with time even as y is increased through its critical value. In other words, n_- does not experience critical fluctuations in the vicinity of the transition, and so can be integrated out of the problem [e.g., perturbatively in the nonlinear terms of the coupled equations (3)]. Asymptotically close to y_1, therefore, Eqs. (3) reduce to a single equation for the order parameter n_+. This equation takes precisely the form (1). Note that the existence of the absorbing state for $y < y_1$ implies that the noise correlations vanish when $n_+(\mathbf{x},t)$ is identically zero; hence

$$\langle \eta(\mathbf{x},t)\eta(\mathbf{x}',t') \rangle \approx \delta(\mathbf{x}-\mathbf{x}')\delta(t-t')n_+(\mathbf{x},t) , \quad (5)$$

as required in the Reggeon theory.[7] (In the absence of any symmetry requirement to the contrary, one assumes that for small n the noise correlations are proportional to the lowest allowed integral—i.e., the first—power of n). Thus the simple two-field approximant to the catalysis model does belong in the Reggeon universality class.

To make this argument more concrete, we now roughly estimate the matrix elements r_{ij} by considering the elementary processes of the underlying microscopic model: First, r_{11} and r_{21} represent the process whereby a single vacancy is filled by a CO molecule, which immediately combines with a neighboring O atom to produce a pair of vacancies. This process proceeds at a rate proportional to y, whereupon $r_{21} = -r_{11} \approx \gamma y$. (Let us now set the rate constant γ to unity by appropriate choice of the unit of time.) Second, r_{22} represents the process whereby a vacant pair is filled by an O_2 molecule; hence $r_{22} \approx -(1-y)$. Finally, r_{12} represents the process whereby one of the sites of a vacant pair is occupied by a CO molecule, which instantaneously combines with a neighboring O atom, producing three vacant sites. In the approximation wherein only individual and pairs of vacancies are considered, these three vacancies are viewed as one vacant pair and one single vacancy. Thus $r_{12} \sim 2y$. Diagonalizing this r_{ij} matrix yields

$$\lambda_{\pm} = [-1 \pm (1 - 4y + 12y^2)^{1/2}]/2. \qquad (6)$$

It is simple to check that λ_+ changes sign at the critical value $y_1 = \frac{1}{3}$, while λ_- is negative for all y. This is in perfect agreement with our general arguments for the model possessing only one field which undergoes critical fluctuations, i.e., for a single-component order parameter.

One can rightly criticize the foregoing analysis on the grounds that it ignores all fields other than single and pair vacancies. For example, there is no good reason to treat triple vacancies as the sum of a single vacancy and a vacant pair, as we have done just above: Triple vacancies (and, indeed, quadruple, quintuple vacancies, and so on) should be treated as fields in their own right, on the same footing as singles and pairs. The small but nonzero density of CO molecules present for all $y > y_1$ should likewise not be ignored. Fortunately, including these (infinitely many) additional fields does not alter the conclusion that the asymptotic critical properties of the oxygen-passivated transition are given by the single-component Reggeon theory. The point is that, again, barring some accidental degeneracy which can occur only with zero probability, the linearized approximant of the coupled equations governing the time evolution of all possible fields in the problem will have just one eigenvalue which changes sign as y increases through y_1. All others will remain negative, so the corresponding eigenfields stay noncritical and can be integrated out of the problem, producing, just as in the two-field theory above, the single-component Reggeon equation.[13] The situation is a familiar one in renormalization-group treatments of critical phenomena in equilibrium systems: Unless there is a symmetry constraining several fields in a given problem to become critical at precisely the same point in the parameter space, then only one of those fields will experience critical fluctuations; the others can be integrated away, having no

influence on the asymptotic critical behavior.

Thus, we conclude that the surface catalysis of the carbon dioxide reaction in the model of Ziff et al. falls in the Reggeon universality class. Though this result rests on the irrelevance for critical behavior of terms higher than quadratic in the field n of Eq. (1)—an irrelevance which can only be carefully demonstrated near the upper critical dimension (i.e., 4)—we find it highly unlikely that such terms are relevant even in two dimensions. The reason is that calculations of critical exponents for the Reggeon theory directly in 2D (Ref. 14) give results in excellent agreement with exponents computed for 2D, discrete-variable lattice models such as directed percolation.[15] Were there extra terms, relevant in 2D, which could be added to the right-hand side of Eq. (1), then one would expect such discrete-variable models (in whose field-theoretic representations these extra terms would surely appear) to belong in a different universality class from the Reggeon theory.

Numerical simulations in 2D by Meakin and Scalapino[2] yield values of 0.69 and 0.61 for the exponents β_{CO} and β_O, which characterize, respectively, the fraction of sites occupied by CO molecules and not occupied by oxygen atoms, just above the transition

$$\langle n_{CO} \rangle \sim (y - y_1)^{\beta_{CO}}; \qquad (7a)$$

$$(1 - \langle n_O \rangle) \sim (y - y_1)^{\beta_O}. \qquad (7b)$$

These results should be compared with the known exponent[6,16] $\beta = 0.586 \pm 0.014$ for the Reggeon model in 2D. (The single-component theory produced by the analysis above clearly predicts $\beta_{CO} = \beta_O = \beta$.) Though the agreement seems marginal, the error bars on β_{CO} and β_O are apparently quite large: Meakin and Scalapino[2] argue that their numerics, in fact, suggest $\beta_{CO} = \beta_O$.

To examine this further, we have computed β and the correlation length exponent[17] ν via a finite size scaling analysis of the Ziff et al. model. We have performed Monte Carlo simulations on 8×8, 16×16, 24×24, 32×32, 48×48, and 64×64 lattices with periodic boundary conditions. For each system, we ran between 200 and 1200 trials, a trial being a single run starting from a blank lattice and running until the system passivates. The coverages prior to passivating and the mean time to passivating were monitored. A finite-size scaling analysis[18] yielded $y_1 = 0.387 \pm 0.001$, and the exponents $\beta_O = 0.63 \pm 0.03$ and[17] $\nu = 0.85 \pm 0.05$. The data for the CO coverage had poorer statistics, since even in the region of the first-order transition only 5% CO coverage is seen, but the resulting critical behavior near the second-order transition appears to be the same as for the oxygen coverage. We find $\beta_{CO} = 0.6 \pm 0.15$. Given the rather small system sizes, we feel that this is fairly strong evidence that the directed percolation model (for which[6,16,17] $\nu = 0.74 \pm 0.01$) describes the critical behavior of the catalysis problem. Thus, it seems likely that the error bars producing the discrepancy between 0.69 and 0.61 in the data of Ref. 2 are large enough to encompass 0.586. Further numerics designed to produce more accurate exponent values are clearly desirable.

Note that the arguments given here generalize straight-forwardly to systems with arbitrary numbers of chemical components. The continuous transitions of any such system into an absorbing state under generic conditions should therefore also belong to the Reggeon universality class.

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