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James W. Evans

Iowa State University, evans@ameslab.gov

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Abstract

The diffusionless ZGB (monomer–dimer) surface reaction model exhibits a discontinuous transition to a monomer-poisoned state when the fraction of monomer adsorption attempts exceeds 0.525. It has been claimed that this transition shifts to $2/3$ with introduction of rapid diffusion of the monomer species, or of both species. We show this is not the case, $2/3$ representing the spinodal rather than the transition point. For equal diffusion rates of both species, we find that the transition only shifts to 0.5951 ± 0.0002 .

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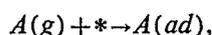
J. W. Evans

Ames Laboratory and Department of Mathematics, Iowa State University, Ames, Iowa 50011

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The diffusionless ZGB (monomer-dimer) surface reaction model exhibits a discontinuous transition to a monomer-poisoned state when the fraction of monomer adsorption attempts exceeds 0.525. It has been claimed that this transition shifts to 2/3 with introduction of rapid diffusion of the monomer species, or of both species. We show this is not the case, 2/3 representing the spinodal rather than the transition point. For equal diffusion rates of both species, we find that the transition only shifts to 0.5951 ± 0.0002 .

Since its introduction in 1986, there has been much interest in the *diffusionless* ZGB (monomer-dimer) surface reaction model,¹ primarily focusing on the "kinetic phase transitions" which it supports.²⁻⁵ In this model, monomers (A) adsorb at single empty sites ($*$) on an infinite square lattice at rate p_A , dimers (B_2) adsorb at adjacent pairs of empty sites at rate $p_B = 1 - p_A$, and different species adsorbed on adjacent sites react instantaneously. Schematically, one has



Here, "g" denotes gas phase and "ad" denotes adsorbed species. The model supports a reactive steady state for $p_1 = 0.391 < p_A < 0.525 = p_2$, and exhibits a continuous transition to a B -poisoned phase at "low" $p_A = p_1$, and a discontinuous transition to an A -poisoned phase at "high" $p_A = p_2$.

In actual surface reactions, diffusion rates for one or more reactant species typically dominate adsorption rates. Such diffusion has the effect of "mixing" adsorbed species, reducing spatial correlations, and validating the traditional "mean-field" treatment of the chemical kinetics. What is perhaps less clear is that such diffusion reduces the effect of fluctuations, thus enhancing metastability and hysteresis.^{4,6} Subsequent studies of the ZGB model have considered (i) the influence of diffusion of $A(ad)$ and $B(ad)$ with equal rates;^{7,8} and (ii) the influence of diffusion of $A(ad)$, with $B(ad)$ still immobile.^{9,10} The motivation for (ii) is in application of this model to the study of CO-oxidation where $CO(ad)$ [represented by $A(ad)$] is highly mobile, and $O(ad)$ [represented by $B(ad)$] is relatively immobile. In both cases, the claim has been made^{8,10} that the discontinuous transition is shifted to the "stoichiometric point" $p_A = 2/3$ (i.e., $p_2 \rightarrow 2/3$), in the regime of large diffusion rates. We show that this is not correct. Instead we find that $p_2 \rightarrow 0.5951 \pm 0.0002$ for (i) through a direct analysis of behavior in this important limiting regime.

Here we concentrate on case (i). The approach of Refs. 7 and 8 is to introduce into the lattice-gas simulations hopping at rate h per adspecies of either type and to determine the shifts in p_1 and p_2 , as h increases. It is found that p_1 quickly decreases to zero for $h \approx 3$, and that p_2 increases toward 2/3. However such calculations are ex-

pensive for large h , and strong metastability leads to overestimation of p_2 , as we describe below. Thus here we adopt the alternative strategy of directly analyzing the high diffusion regime, noting that large diffusion rates of *both* species ensure simple mean-field behavior is displayed. Henceforth, we denote concentrations or coverages of $A(ad)$ by A , and of $B(ad)$ by B .

We consider first the kinetics for a system which is spatially homogeneous. For infinite reaction rate, in the limit of diverging hop rate, h , there can only be one type of reactant species present on the surface at any time. Suppose first that this species is A . Then since the adsorption rate of A is $p_A(1-A)$, and that of B is $p_B(1-A)^2$ (given the adlayer is random), it follows that

$$d/dt A = p_A(1-A) - 2p_B(1-A)^2. \quad (1)$$

Thus for $p_A/p_B > 2$, one finds that $A(t) \rightarrow 1$ for any initial value, $A(0)$, of A . For $p_A/p_B \leq 2$, one finds that $A(t) \rightarrow 0$ if $A(0) < 1 - \frac{1}{2}p_A/p_B$ (and thereafter B increases as described below), $A(t) \rightarrow 1$ if $A(0) > 1 - \frac{1}{2}p_A/p_B$, and $A(0) = 1 - \frac{1}{2}p_A/p_B$ corresponds to an unstable steady state. If B is the species present on the surface, then clearly

$$d/dt B = 2p_B(1-B)^2 - p_A(1-B). \quad (2)$$

Thus for $p_A/p_B > 2$, one finds that $B(t) \rightarrow 0$ if $B(0) < 1$ (and thereafter A increases as described above). For $p_A/p_B \leq 2$, one finds that $B(t) \rightarrow 1 - \frac{1}{2}p_A/p_B$ for any $B(0) < 1$. In conclusion, it is clear that this model exhibits bistability in the region $0 < p_A/p_B < 2$ or $0 < p_A < 2/3$ (see Fig. 1). From general properties of bistable systems,¹¹ or from the specific mean-field analysis of the monomer-dimer reaction with finite reaction rate,⁶ one expects the equistability point, $p_A = p_e$, in this system to occur in the interior of the bistability range, i.e., below the upper spinodal point, $p_A = 2/3$. This equistability point, p_e , will correspond to the first order transition, p_2 , in the lattice-gas model in the limit as $h \rightarrow \infty$.

Determination of p_e requires a reaction-diffusion equation analysis^{6,11} of spatially inhomogeneous systems. We emphasize that in the limit of diverging hop rate, h , the spatial inhomogeneity occurs on a "macroscopic" length scale $O(h^{1/2})$ (diverging relative to the lattice spacing " a "). Specifically we analyze the evolution of chemical or trigger waves separating the poisoned phase α ($A=1$, $B=0$) and the reactive phase β ($B=1 - \frac{1}{2}p_A/p_B$, $A=0$):

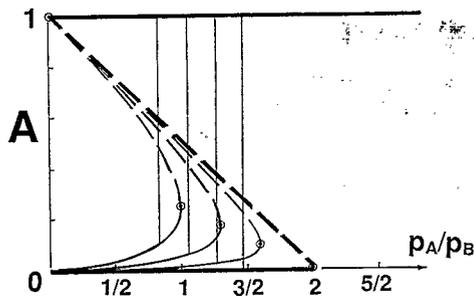


FIG. 1. Dependence of A on p_A/p_B in the steady state of the monomer-dimer ($A+B_2$) reaction for reaction rates $k=1, 3, 12$, and ∞ (from left to right). Solid (dashed) curves indicate stable (unstable) states. For this model, stable state B value equal unstable state A values. Fine vertical lines indicate equistability points.

β displaces α for $p_A < p_e$, α displaces β for $p_A > p_e$, and a stable kink between α and β is formed when $p_A = p_e$. Because of the "singular" nature of the infinite reaction rate problem, we have chosen to determine p_e for the analogous mean-field monomer-dimer reaction problem with finite reaction rate, k , and then to extrapolate to $k = \infty$. The appropriate reaction-diffusion equations are described in detail in Ref. 6. Here we just note that the conventional form (obtained by adding Laplacian diffusion terms to the rate equations) fails to account for the influence on the diffusion of one species of the mere presence of the other (via site blocking). Nonlinear corrections must be included to account for this effect. We use both conventional and modified equations to determine p_e , and note that as $k \rightarrow \infty$ their predictions must coincide (since here A and B cannot coexist at the same macroscopic point on the surface). Our results for p_e vs k are shown in Table I, and the corresponding stable kink profiles for two k values are shown in Fig. 2. Since the upper spinodal point satisfies $p_A \sim 2/3 - 2^{2/3} 3^{-5/2} \cdot k^{-1/2}$, as $k \rightarrow \infty$, we extrapolate our data using $p_e \sim a + b \cdot k^{-1/2} + \dots$ to obtain $p_e(k = \infty) = p_2(k = \infty) = 0.5951 \pm 0.0002$.

It is also instructive to consider directly the reaction-diffusion equations for $k = \infty$. Then using a conventional treatment of diffusion (with coefficient $D \propto a^2 h$), in the region where $A > 0$, one has

$$\partial/\partial t A = p_A(1-A) - 2p_B(1-A)^2 + D\partial^2/\partial x^2 A. \quad (3)$$

For the stable kink profile, A is independent of t , and (3) can be written in pseudo-Newtonian form as

$$D d^2/dx^2 A = -\partial/\partial A V(A),$$

where

TABLE I. Values of p_e for various k , determined via reaction-diffusion equations with conventional (C) and modified (M) treatments of diffusion, as described in Ref. 6.

k	1	3	12	49	196	784
C	0.456	0.514	0.560	0.5806	0.5892	0.5924
M	0.444	0.502	0.555	0.5780	0.5878	0.5919

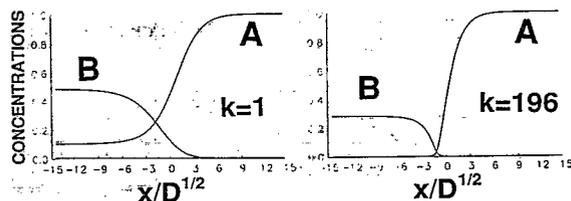


FIG. 2. Concentration profiles for the stable kink separating reactive and poisoned steady states at the equistability point. Profiles for reaction rate $k=1$ and $k=196$ are shown.

$$V(A) = 2p_B(1-A)^3/3 - p_A(1-A)^2/2. \quad (4)$$

In the kink profile, A starts at zero at $x = x^*$, say, and evolves to unity as pseudo-time $x \rightarrow \infty$ (inset of Fig. 3). Since $p_A/p_B < 2$, this corresponds to initially traveling downhill from $V(0)$, and then uphill just reaching the unstable maximum $V(1) = 0$, in the potential $V(A)$ (Fig. 3). Since the initial pseudo-velocity $dA/dx(x = x^*)$ must be non-negative (inset of Fig. 3), this dynamics can only be achieved if $V(0) \leq 0$ so $4/3 \leq p_A/p_B < 2$ which greatly limits the range of possible values for $p_e(k = \infty)$. One then has $(1/2)D[dA/dx(x = x^*)]^2 + V(0) = 0$, by conservation of pseudo-energy, so $dA/dx(x = x^*) = D^{-1/2}(p_A - 4p_B/3)^{1/2}$. From a similar analysis of kink profile in the region where $B > 0$, one finds that $dB/dx(x = x^*) = -D^{-1/2}(p_A^3 p_B^{-2}/12 - p_A + 4p_B/3)^{1/2}$. Given $p_e(k = \infty)$ above, we can thus readily determine the entire $k = \infty$ kink profile including concentration slopes at $x = x^*$. This approach was used to determine the profile shown in the inset of Fig. 3.

It is appropriate here to indicate why the simulation study of Ref. 8 overestimated p_2 (or p_e) for large diffusion rates, h . For any $h \geq 0$, there exists in the lattice-gas model a metastable reactive state for $p_2 \leq p_A \leq p_s$, say, where p_s denotes the upper spinodal point. Simulations starting with an initially empty lattice, for p_A slightly above p_2 in this range, tend to get stuck in the metastable state rather than reaching the true A -poisoned steady state. This has led to overestimates³ of p_2 even for $h = 0$, where^{5,12} $p_2 = 0.525$ and

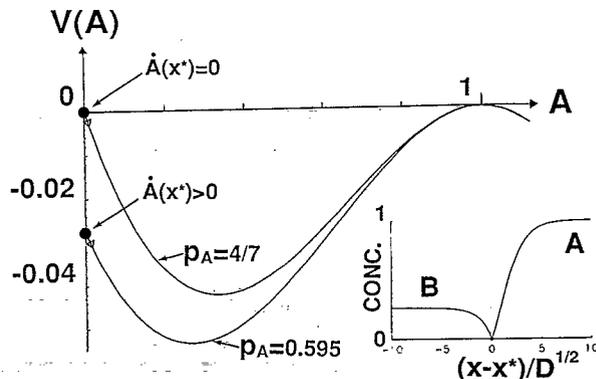


FIG. 3. Potential, $V(A)$, describing the A -profile or "dynamics" of the kink at the equistability point when $k = \infty$ (see inset). We indicate that the initial "speed" $\dot{A}(x = x^*) = dA/dx(x = x^*)$ required to just reach the local maximum at $A = 1$ is positive for $p_A > 4/7$.

$p_s=0.529$. As $h \rightarrow \infty$, metastability increases and $p_s \rightarrow 2/3$ making it even more difficult to reach the true steady state. Of course, with long enough simulation runs, one can always reach the true steady state. This appears to have been the case in Ref. 7, where extrapolation of their p_2 estimates to $h = \infty$ yields a value of 0.595 ± 0.003 consistent with our more precise analysis. They however do not comment on limiting behavior. It should also be noted that alternative simulation techniques are now available^{4,5} which avoid metastability problems in the determination of p_2 .

Finally, we briefly comment on case (ii), where only the diffusion rate of $A(ad)$ becomes large, but where it has also been claimed¹⁰ that $p_2 \rightarrow 2/3$. Unlike case (i), this regime cannot be described by simple mean-field theory since nontrivial correlations persist in the B -adlayer statistics. This leads to nontrivial dependence of B on p_A in the reactive steady state. Detailed analysis of the appropriate "hybrid model" for this regime will be described elsewhere.¹³ Here we note however that the analysis of case (i) with only A on the surface still applies. Consequently this model still is bistable over the range $0 < p_A/p_B < 2$, with stable and unstable state values of A as in (i). Thus the equistability point, $p_e = p_2$, in the limit of infinite diffusion rates, should be strictly less than the upper spinodal value

of $p_A = 2/3$. As for case (i), simulation estimates of p_2 can be easily corrupted by strong metastability.

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