

Trigger waves in a model for catalysis

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We consider the model of catalysis due to Ziff, Gulari, and Barshad [Phys. Rev. Lett. **56**, 2553 (1986)] as a pattern formation problem. We find that the model supports trigger waves, and we examine the dependence of the wave velocity on diffusion. In addition to the usual interface width, there is a statistical broadening of the wave front that increases in time as $t^{1/3}$.

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I. INTRODUCTION

Chemical reactions driven out of equilibrium display a wealth of phenomena, including pattern formation of many types. Some aspects of chemical patterns can be understood from reaction-diffusion equations built from the usual rate equations, with the addition of a diffusion term [1]. This approach has had great success in predicting and understanding many features. However, for some effects deterministic, coarse-grained equations are not an adequate approximation. This paper introduces Monte Carlo techniques in this context in order to model the effect of fluctuations and correlations on the patterns.

One of the best studied and simplest Monte Carlo models in nonequilibrium chemistry is the monomer-dimer model for catalysis of Ziff, Gulari, and Barshad (ZGB) [2]. It was introduced to study the oxidation of carbon monoxide on a platinum substrate. In this Monte Carlo model a lattice of sites can either be unoccupied, occupied by A (which could represent CO), or occupied by B (O). At each Monte Carlo step, a site is chosen randomly. If it is empty, an attempt is made to adsorb either A or B_2 . B_2 adsorption requires two adjacent empty sites, each of which captures one B atom, while A requires but one empty site. If an A lands next to B or vice versa, they both react, and both sites empty. The control parameter, y , is the probability that an adsorbing particle will be A or B_2 . y is related to the partial pressures of gas phase A and B_2 .

ZGB and others [3] found large deviations from mean-field rate equations. In simulations the model has two phase transitions: a continuous transition between a B poisoned phase and a reactive phase at $y = 0.389$, and a first-order transition between a reactive phase and a A poisoned phase at $y = 0.525$. (Poisoned means totally covered so that no more adsorption is possible.) In the vicinity of the first-order transition there are metastable

states, and the system shows hysteresis. [2] The reactive phase has a moderate concentration of B , and very little A . Although the simplest rate equation is unsuccessful for ZGB, more complex mean-field theories that include some correlations have been given [4,5].

Experiments [6–8] have shown that the real catalysis of CO and O₂ on platinum has steady states similar to the A poisoned and reactive phases of the ZGB model. There is an important difference between the experiments and ZGB: real systems do not show O poisoning or anything comparable to the second-order transition. For this paper, we will concentrate on the parameter range near the first-order transition to A poisoning, which does occur in experiment: An abrupt transition to CO poisoning is clearly seen, for example, in Ref. [8]. Of course, in a real experiment, *complete* poisoning does not happen. There is a finite probability of, for example, thermal desorption of CO. This can be accommodated in the model: It is known that a small desorption probability of A has no qualitative effect on the first-order transition [3]. All the results of this paper are insensitive to desorption of A . For small y , the effect of desorption is large.

Experiments on the dynamics of the reaction showed patterned structures, including trigger waves, target patterns, and spiral waves. There has been considerable work on these structures using reaction-diffusion equations [5,6]. In this paper, we will study chemical waves of this type, directly in terms of the ZGB model. Our motivation is that reaction-diffusion equations and other mean-field treatments lack noise and spatial correlations which ZGB has, and which could affect chemical waves.

Spatial correlations in the ZGB model have been shown to affect its behavior. For example, the reaction rate in the model is not given by the mean-field expression $Q \sim \rho_A \rho_B$ [9]. This is because correlations produce patches [10] of A and B and the reaction can only take place at the boundary of the patches. Real systems in two dimensions should show this effect as well. There is

clearly also noise in ZGB, namely, shot noise in the flux of added particles and internal noise from the stochastic nature of the reaction. This is the focus of the present work.

There have been other studies of chemical waves using Monte Carlo simulations some time ago [11]. Another approach, that of lattice-gas cellular automata [12] does include some of the effects that we consider, and it has been applied to spiral waves. Since a preliminary account of this work appeared [13] a very similar approach to trigger waves was given by Evans and Ray (ER) [14]. There are some differences in our approaches, which will be pointed out below.

In the next section, we study the ZGB model in the bistable regime and demonstrate trigger wave propagation. We investigate the velocity of the front and show how it depends on y and the diffusion rate of adsorbed A . (We assume negligible B diffusion because in experimental systems, O is much more tightly bound to the surface than CO [6]. Note that in ER the diffusion was taken to be the same for A and B .) We find evidence of an effective diffusion constant, even in the absence of an explicit diffusion. The width of the front is shown to increase in time in contrast with the reaction-diffusion result. This effect of noise can be understood quantitatively using the theory of interface kinetics [17]. We show by explicit simulation that the ZGB model does fall in the same universality class as other interface problems, and we comment on when this behavior might be expected to fail.

This calculation is for a highly idealized model system, and the relationship of this work with real catalysis (if any) is not clear. It would be extremely interesting if we could find a system in which these statistical effects are important and could be observed. For the moment we have only very tentative suggestions to give about the possibility of such observations, which are given in the last section of the paper.

II. TRIGGER WAVES: VELOCITY

A bistable medium is an extended dissipative system with a stable state and a metastable state. At a flat boundary between the two, the metastable state will lose ground before the stable one, and the boundary will move. This is a trigger wave.

We do ZGB simulations with A diffusion [3]: we make D attempts to move a randomly chosen site between each

adsorption attempt. A diffusion attempt is successful if the site chosen has an A and an adjacent empty site in a randomly chosen direction. We create a front by putting a barrier in the system and preparing two different states: one side starts poisoned with A and the other with a finite coverage of B . Adsorption with the same values of y causes the two halves to develop into separate metastable states, one of high A occupancy and low reaction rate, the other of low A occupancy and high reaction rate. Then we remove the barrier and a wave front propagates. A typical front is shown in Fig. 1.

We measure the velocity of the front by tracking the x position of the front center, defined as the locus of 50% A coverage. The width is defined as the distance between the x positions of 10% and 90% A occupancy. The dependence of velocity on y and on D is shown in Fig. 2(a). The time unit in this graph is the conventional one in Monte Carlo simulations, namely, $\Delta t = 1$ corresponds to one adsorption attempt per site of the lattice; this defines our unit of time, τ , as a characteristic time for the process. The y at which the front is stationary, y_c , increases with increasing D as has been found in earlier studies [15].

We fit our data with:

$$v = \alpha \sqrt{D_e} [y - y_c(D) + O((y - y_c)^2)], \quad (1)$$

in which D_e is an effective diffusion constant. We use this form because reaction-diffusion equations show that velocity should vary as the square root of the diffusion constant [1], $v_0 \approx \sqrt{D/\tau}$. As pointed out by, for example, Clement *et al.* [10], in driven reactive systems, there is a reaction driven effective diffusion in addition to any explicit diffusion. We therefore expect $D_e = D + D_0$, where D is the number of diffusion steps and D_0 is of order unity in units of a^2/τ , where a is the lattice constant. The dependence on y is a power series expansion around y_c . We find D_e by noting that the slope of the line $\Delta v(y)/\Delta y$ is $\alpha \sqrt{D_e}$. A plot of $[\Delta v(y)/\Delta y]^2$ vs D is shown in Fig. 2(b). We fit D_e as $D_e = D + D_0$, where D_0 is a reaction driven diffusion constant of about 3. This value is seen in Fig. 2(b) from an extrapolation to (unphysical) negative values of D .

Note that all of the curves for different D seem to meet at $y_0 \simeq 0.576$. At this value, v is independent of D and is presumably the mean-field value. Our "mean-field" behavior is different from that of ER because the asymmetric diffusion that we adopt complicates the interpretation.



FIG. 1. Trigger wave front. Empty cells are white, B is gray, and A is black. The A poisoned phase on the bottom and the reactive phase on the top are separated by the front. Individual lattice sites can be seen in this relatively small simulation.

This unexpected feature implies a simple behavior for $y_c(D)$, namely, that $y_c(D) = y_0 - K/\sqrt{D + D_0}$, where K is a constant. We have been unable to find a derivation for this peculiarity of the ZGB model.

III. TRIGGER WAVES: INTERFACE WIDTH

In a deterministic system described by reaction-diffusion equations, the interface between the stable and metastable regions should be of fixed width [1], $w_0 \approx \sqrt{D\tau}$. This width corresponds to the mixed region near

the front, which is visible in Fig. 1. Our system has an extra source of broadening, statistical fluctuations, which leads to *wandering* of the front [16], which is also visible in Fig. 1. We describe the extra width, w , by appealing to the theory of kinetic roughening: If a front $x(y, t)$ moves in the presence of noise, the usual equation of motion is the KPZ equation [17]

$$\frac{\partial x}{\partial t} = \eta(y, t) + v + \nu \nabla^2 x + \frac{1}{2} \lambda (\nabla x)^2, \quad (2)$$

where η is white noise with zero mean such that $\langle \eta(x, t) \eta(y, s) \rangle = \sigma \delta(x - y) \delta(t - s)$ and v is the front

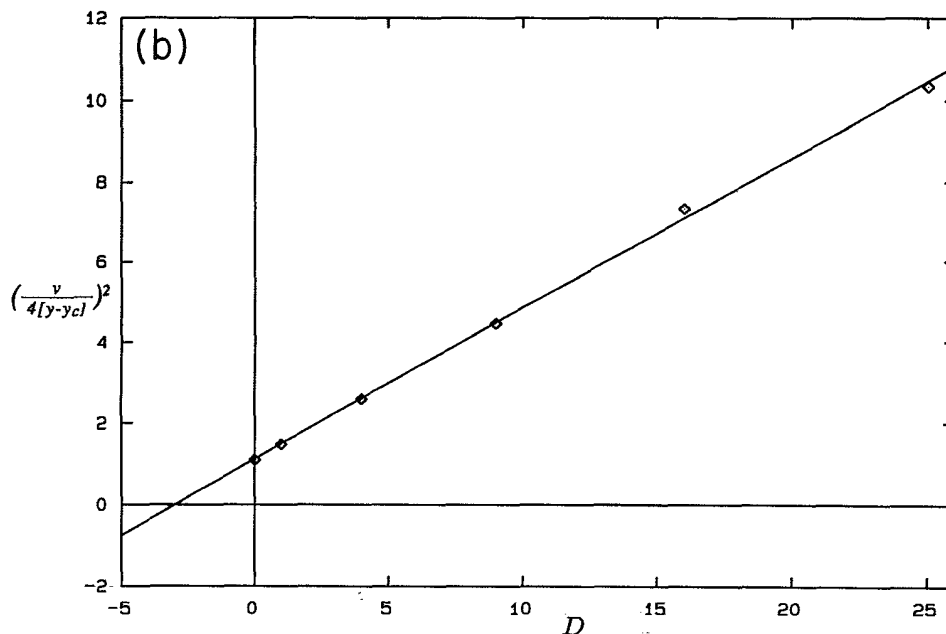
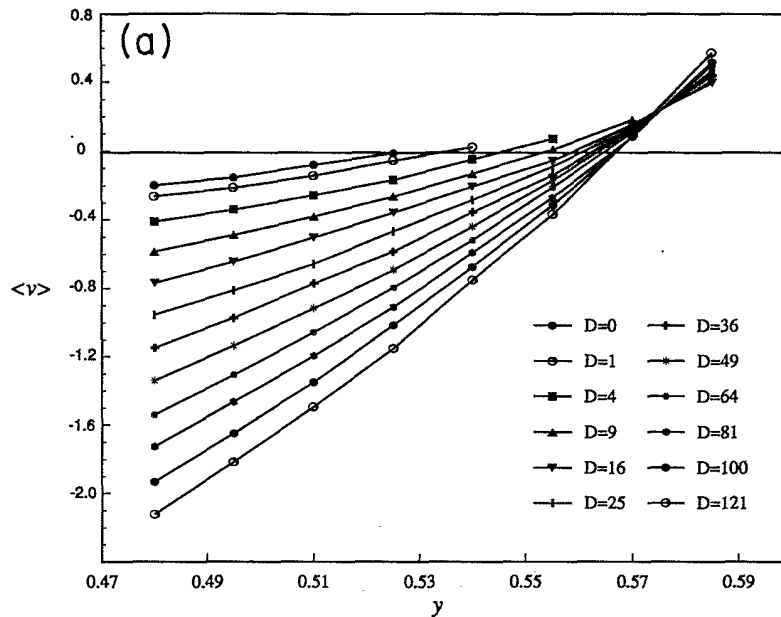


FIG. 2. (a) Average velocity v [units (lattice constants)/ τ , where τ is defined in the text] vs y for various D . Simulation on a 50×100 lattice averaged over 25 runs. (b) $[\Delta v(y)/\Delta y]^2$ vs D . The intercept with the horizontal axis is $-D_e$.

velocity discussed above.

The KPZ equation was originally used for surface growth problems, but it is very general and should apply here. It is the simplest local equation consistent with the symmetries of the problem, namely, that there be reflection symmetry in the plane of the surface, and translation symmetry in x . Noise arises from inhomogenieties in the reactants induced by shot noise. Higher order terms can be neglected for sufficiently large coarse-grained surfaces.

It has been known for some time that the behavior of the width is summarized in a scaling formula [18] involving critical exponents α, β, z :

$$w = t^\beta f(t/L^z) = \begin{cases} C_t t^\beta, & \text{if } t \ll L^z; \\ C_L L^\alpha, & \text{if } t \gg L^z, \end{cases} \quad (3)$$

where $\alpha = \beta z$, and L is the size of the system in the y direction. The saturation of the width is a size effect: the fluctuations stop increasing the width when they are correlated over the whole interface. In 1 + 1 dimensions, one expects [18] $\beta = 1/3, \alpha = 1/2$, so that $w \sim t^{1/3}$ unless $\lambda = 0$; then, the width increases as $t^{1/4}$ (Edwards-Wilkinson growth [19]). Furthermore, in this case [20] the amplitudes, C_t, C_L , are known:

$$C_t^2 = \begin{cases} \sigma/\sqrt{2\pi\nu}, & \text{if } \lambda = 0; \\ 0.4(C_0^2\lambda)^{2/3}, & \text{if } \lambda \neq 0, \end{cases} \quad (4)$$

$$C_L^2 = C_0/12, \quad (5)$$

where $C_0 = \sigma/2\nu$ is a characteristic parameter that is invariant under coarse graining [18,21].

We can show that $\lambda = v$ from a simple geometrical argument [17]. This is because in this problem there is no preferred direction in space: a front can only grow normal to its local direction, say, by $v\delta t$. Now suppose the normal is tilted by θ , with respect to the s direction as defined by the overall channel. Then $\delta x = [v\delta t]/\cos(\theta) \approx [v\delta t][1 + \theta^2/2] \approx [v\delta t][1 + (\nabla x)^2/2]$. Thus, a stalled front, $v = \lambda = 0$, should exhibit Edwards-Wilkinson roughening but a moving one should exhibit KPZ roughening. This general argument should hold for any model without special symmetries, and assumes only that the correlations do not extend over the whole length of the channel. (This point was also made by ER.)

In Fig. 3 we plot the interface width as a function of time for interfaces of different size, L , for a rapidly moving front, $y = 0.45, v = 0.3$. The expected behavior, including finite-size saturation, is found. The growth of w with t is inconsistent with the predictions of reaction-diffusion equations, but it does have the power law scaling of KPZ behavior. The plot gives a best fit with a $\beta \approx 0.30$.

We can go further and estimate all the parameters in the KPZ equation from our data. Using the saturated values for w in Fig. 3 we find $C_0 \approx 10.8$. Also, the prefactor of t^β is approximately 2.1. Comparing these numbers with Eq.(5) we find $\lambda \approx 0.3$ in excellent agreement with the directly measured velocity. If we guess that $\nu \sim D_e$ we have numerical values for all the parameters. Unlike C_0 and λ , ν does change under coarse

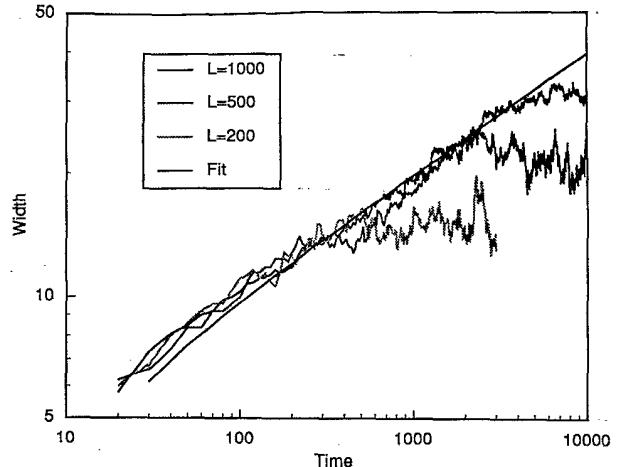


FIG. 3. Front width, w , vs time on lattices of various sizes, L , both in units of the lattice constant. The finite size saturation is evident for $L = 200$.

graining [21].

Kang and Weinberg studied a different model than ours (the $A + B \rightarrow 0$ reaction). In this case, if there is interparticle repulsion they found $w \sim t^{1/4}$ and concluded that $\lambda = 0$ [22]. It is not clear to us why this should be so for their model, or whether it exhibits bistability of the same type as ZGB. It may be that the velocity of their interface was simply too small to see the effect of the nonlinear terms.

In fact, we expect the crossover to KPZ behavior to take place when $w_{\lambda=0} \sim w_{KPZ}$, i.e., when $t_c \approx 63\nu^5/\sigma^2\lambda^4$, which can be very large when λ is small. However, for our parameters this time is of order 500, again in agreement with the plot of Fig. 3.

There is, however, an assumption in this discussion which is not obviously valid, namely, that the fluctuations are confined to the interface. In our particular case we have ensured that this be so by our choice of conditions: there are *no* fluctuations in the bulk of the poisoned A phase, so that surface fluctuations are well defined. However, if we were to allow our interface to progress in the opposite direction by tuning y above the stall point, or if we were to allow A desorption, we should expect an interference between surface and bulk fluctuations: the surface could advance by jumps to engulf islands in the metastable phase. We might expect a crossover to something like invasion percolation. We intend to pursue this subject further in future publications.

IV. SUMMARY AND DISCUSSION

In this work, we have attempted to join two strands of work on catalytic process, namely, statistical modeling and deterministic modeling by reaction-diffusion equations. We have shown that there are trigger waves in the ZGB model. We have shown that statistical processes should affect the interface width of trigger wave fronts.

We see no *a priori* reason why statistical wandering could not be observed in some conditions, though in the

usual regime of length and time scales of ultrahigh vacuum (UHV) experiments [6,7], such effects are clearly negligible. For large D the intrinsic width w_0 will be larger than w , except for a crossover at very long times or large scales.

We can estimate the crossover as follows: we ask when the $w_0 \sim \sqrt{D\tau}$ is of the order of the wandering on some length scale: $w \sim \sqrt{C_0 L}$. This implies that $L \gg D^2\tau/\sigma$. We can estimate σ by noting that for the shot-noise induced processes that interest us, $\sigma \sim a^3/\tau$, where a is an atomic dimension. (For our lattice model $\sigma \sim 60$.) Replacing D by a^2/τ_h , where τ_h is a hopping time, we find that we need $L/a \gg (\tau/\tau_h)^2$. Since the rate-limiting process in the UHV experiments is adsorption which takes place at times of order 1 monolayer/sec, and $\tau_h \sim 10^{-8}$ sec for typical diffusion constants, this observation is vastly out of the question.

However, it is not necessary to do the experiment in UHV. Recently, for example [24], waves of the sort that interest us were observed at atmospheric pressures with characteristic times which are probably six to eight orders of magnitude smaller than in the UHV experiments. It would be extremely interesting to see whether noise-induced roughening of chemical interfaces could be observed in these conditions. However, very considerable further work will be required needed to clarify this point, and for the moment our suggestion should be viewed as speculative. In particular, the role of inhomogeneity of the substrate and gas phase couplings should be investigated, and a more careful estimate of the relevant crossover length scale is needed.

In real catalytic systems, more complicated waves such as spiral patterns have been seen [6]. These arise when a slow reaction such as reconstruction of the substrate is coupled to the chemical reaction. We have preliminary results [23] (see Fig. 4) showing that this can be represented in a Monte Carlo simulation of the type used here by introducing a slow variable at each site which has two



FIG. 4. Spiral wave generated by adding a slowly relaxing variable at each surface site. Empty cells are white, B is gray, and A is black.

values, α and β . An α phase site not occupied by A has a small probability per Monte Carlo step of changing to β and a β site occupied by A slowly changes to α . In addition, we disallow B adsorption on the β sites, and allow a finite probability of desorption of A . This is a crude representation of what happens when a platinum surface reconstructs [6]. A simulation of this type could cast light on the noise-induced nucleation of spiral patterns, though, again, the conditions necessary to see our effects are very different from those of these experiments.

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