# Kinetics of the monomer-monomer surface reaction model

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The two-dimensional monomer-monomer ($AB$) surface reaction model without diffusion is considered for infinitesimal, finite, and infinite reaction rates $k$. For equal reactant adsorption rates, in all cases, simulations reveal the same form of slow poisoning, associated with clustering of reactants. This behavior is also the same as that found in simulations of the two-dimensional *voter model* studied in interacting-particle systems theory. The voter model can also be obtained from the dimer-dimer or monomer-dimer surface reaction models with infinitesimal reaction rate. We provide a detailed elucidation of the slow poisoning kinetics via an analytic treatment for the $k=0^+$ $AB$ reaction and the voter models. This analysis is extended to incorporate the effects of place-exchange diffusion which slows, but does not prevent poisoning. We also show that the $k=0^+$ $AB$ reaction with no diffusion is equivalent to the voter model with diffusion at rate $\frac{1}{2}$. Identical behavior of the monomer-monomer reaction and the voter model is also found in an "epidemic" analysis, where one considers the evolution of a surface poisoned by one species, except for a small patch. Finally, we apply our findings to elucidate the behavior of the monomer-dimer surface reaction model for small reaction rates.

## I. INTRODUCTION

In this contribution, we shall consider the monomer-monomer (or $AB$) surface reaction model,

$$A(\text{g})+* \rightarrow A(\text{ad}) , \quad B(\text{g})+* \rightarrow B(\text{ad}) ,$$
$$A(\text{ad})+B(\text{ad}) \rightarrow AB(\text{g})+2* , \tag{1}$$
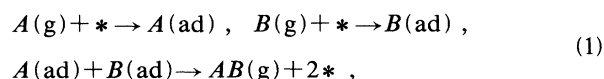
on a square lattice of adsorption sites. Here g and ad denote gas-phase and adsorbed species, and * denotes an empty surface site. Adsorbed species are immobile unless otherwise stated. Adsorption rates $p_A$ and $p_B$ for $A$ and $B$, respectively, are normalized so that $p_A+p_B=1$, and the reaction rate is denoted by $k$. We shall consider the reaction-limited regime with infinitesimal reaction rate $k=0^+$, the regime of finite reaction rates $0<k<\infty$, and the adsorption-limited regime with infinite reaction rate $k=\infty$.

The basic behavior of these models follows from inspection of the appropriate *exact* rate equations for the evolution of concentrations or coverages of $A$(ad) and $B$(ad) with time $t$. Here we let $[A]$ and $[B]$ denote the concentration (i.e., coverage) of $A$(ad) and $B$(ad), $[E]=1-[A]-[B]$ denote the concentration of empty sites, $[AB]$ denote the probability of finding an adjacent $A$(ad)$B$(ad) pair as distinct from a $B$(ad)$A$(ad) pair, $A'$ denotes a site not filled by $A$, and $[A']=1-[A]$ denote the corresponding probability, etc. The presence of correlations implies that $[AB]\neq[A][B]$, $[EE]\neq[E]^2$, etc. For a square lattice, one immediately obtains for $0<k<\infty$

$$\frac{d[A]}{dt}=p_A[E]-4k[AB] , \quad \frac{d[B]}{dt}=p_B[E]-4k[AB] ,$$

so

$$\frac{d}{dt}([A]-[B])=(p_A-p_B)[E] . \tag{2}$$

For $k=\infty$, clearly one has $[AB]=0$. Here it is convenient to let

$$D(A)=p_A \begin{bmatrix} & B' & \\ B' & E & B' \\ & B' & \end{bmatrix} , \quad D(B)=p_B \begin{bmatrix} & A' & \\ A' & E & A' \\ & A' & \end{bmatrix}$$

denote nonreactive adsorption or deposition rates for $A$ and $B$, respectively. The quantities in the square brackets denote the probabilities of finding an empty site with none of the neighboring sites occupied by $B$'s for $D(A)$ or by $A$'s for $D(B)$. Then $T(J)=p_J[E]$ and $R(J)=T(J)-D(J)$ denote total and reactive adsorption rates for $J=A$ or $B$, respectively. Thus for $k=\infty$ one has

$$\frac{d[A]}{dt}=D(A)-R(B) , \quad \frac{d[B]}{dt}=D(B)-R(A) ,$$

so

$$\frac{d}{dt}([A]-[B])=(p_A-p_B)[E] , \tag{3}$$

the last result being identical to (2). Finally, let $\tau=kt/(1+k)$ and consider the limit $k=0^+$ where one obtains [1]

$$\frac{d[A]}{d\tau}=-\frac{d[B]}{d\tau}=4(p_A-p_B)[AB] . \tag{4}$$

In all cases, it is immediately clear that if $p_A \neq p_B$, then the only steady state is a trivial "adsorbing" poisoned state with $[E]=[AB]=0$ and $[A]=1$ or $[B]=1$. Note that adding diffusion to these models does not change rate equations (2)–(4) for the species concentrations, so the same conclusion applies. Although it does not

rigorously follow from (2)–(4) alone, one might expect that poisoning by the species with the larger pressure occurs exponentially with the rate proportional to $(p_A - p_B)^{-1}$. This claim is supported by simulations [2].

Henceforth, our attention naturally focuses on the case where $p_A = p_B = \frac{1}{2}$, and where (2)–(4) provide no direct information about the steady state. In an important early simulation study of the reaction-limited regime $k = 0^+$, Wicke et al. [3] noted a propensity for reactant clustering or segregation, and gave a simple argument for this propensity. A detailed study of analogous reactant segregation for the adsorption-limited regime $k = \infty$ was given by Ziff and Fichthorn [4]. Although a reactive steady state appears to form in these systems, more detailed studies revealed that reactant clusters continue to slowly grow or coarsen, while the reaction rate correspondingly slowly decreases to zero [2,5]. We discuss this behavior in detail below. It is, however, appropriate to note here that Ben-Avraham and co-workers [6,7] argue that this slow poisoning is driven by concentration fluctuations of a diffusive nature. They also show that the mean poisoning time for these models, on a finite (two-dimensional) lattice of $N$ sites, increases roughly linearly with $N$. (The precise form is like $N \ln(N)$ [8].) This contrasts the behavior of processes with a true reactive steady state (on an infinite lattice), where the mean poisoning time increases exponentially with $N$ [6,7].

A primary focus of this contribution is to compare the above behavior for the monomer-monomer reaction with that of the voter model studied extensively in interacting particle systems theory [9]. In the voter model, sites have two states or "opinions," $A$ or $B$, say. Each site waits an exponential time, with parameter 1, say, at which time it changes its opinion to that which it "sees" on a randomly chosen neighboring site. Another realization of this model is as a dimer-dimer surface reaction with infinitesimal reaction rate: imagine a surface completely covered with $A$ and $B$; the reaction $A(\text{ad}) + B(\text{ad}) \rightarrow AB(\text{g}) + 2*$ occurs at a randomly chosen $A(\text{ad})B(\text{ad})$ pair, and the resulting empty pair is immediately filled with an $A_2$ dimer $A_2(\text{g}) + 2* \rightarrow 2A(\text{ad})$, or a $B_2$ dimer $B_2(\text{g}) + 2* \rightarrow 2B(\text{ad})$, with equal probability. The feature that the voter model has only trivial "poisoned" steady states in $d \leq 2$ dimensions (i.e., consensus is eventually reached) has been established rigorously. This was achieved by relating the voter model to an auxiliary problem of coalescing random walks, and then using the recurrence property of random walks [10]. The lack of existence of nontrivial steady states indicates that clustering must occur. We emphasize, however, that the kinetics of clustering, e.g., the time decay of the concentration [$AB$] of neighbors with opposite opinions, apparently has not been well characterized to date. We shall comment further on the properties of the voter model below.

In Sec. II we present simulation results characterizing and comparing the slow poisoning kinetics for the monomer-monomer reaction and the voter model (without diffusion). Analytic elucidation of this behavior is presented for the $k = 0^+$ monomer-monomer reaction and for the voter model. In Sec. III we consider the evolution of a surface which is initially covered or poisoned

by one species ($B$, say), except for a small patch. We then explore how the probability that the system is not completely poisoned by $B$ varies (decreases) with time. This type of question is familiar in theories of "critical epidemics" [11], and has been considered previously within the context of surface reaction models [5,12]. The effect of adding diffusion to the $k = 0^+$ monomer-monomer reaction and the voter model is considered analytically in Sec. IV. We apply the findings of Sec. III to elucidate the behavior of the monomer-dimer surface reaction for low reaction rates [5,13–15] in Sec. V, and provide some concluding remarks in Sec. VI.

## II. POISONING KINETICS

We first present results for poisoning kinetics for the monomer-monomer reaction with $p_A = p_B = \frac{1}{2}$ and for the voter model (without diffusion). We start from an initially empty lattice for $k > 0$ and from a random distribution with $[A] = [B] = \frac{1}{2}$ for $k = 0^+$. In order to present a unified description, we examine the behavior of the concentration $[AA']$ of adjacent pairs of sites, one filled with $A(\text{ad})$ and the other not. Thus one has $[AA'] = [AB]$ when $k = 0^+$, $[AB] + [AE]$ when $0 < k < \infty$, and $[AE]$ when $k = \infty$. A unified and well-defined time scale is provided by $\tau = kt/(1 + k)$ for $0^+ \leq k \leq \infty$. Simulations were performed involving about 40 trials on a $200 \times 200$ lattice up to $\tau = O(10^3)$. A typical time per trial on a Silicon Graphics machine is 3 h. To test the relationship $[AA'] \sim \tau^{-\omega}$, as $\tau \rightarrow \infty$, we plot $\log_{10}([AA'])$ against $\log_{10}(\tau)$ in Fig. 1. From the data for $O(10^2) \leq \tau \leq O(10^3)$, we find effective exponent values of $\omega = 0.04$–$0.08$ for the monomer-monomer reaction with various $k$ (Table I) and a voter model value of $\omega = 0.096$. These values are consistent with previous estimates for special cases [2,5]. It has also been proposed [2] that $[AA'] \sim \log_{10}(\tau)^{-\sigma}$ as $\tau \rightarrow \infty$, so in Fig. 2 we plot $\log_{10}([AA'])$ against $\log_{10}(\log_{10}(\tau))$. We thus find for $O(10^2) \leq \tau \leq O(10^3)$ effective exponent values of $\sigma = 0.25$–$0.5$ for the
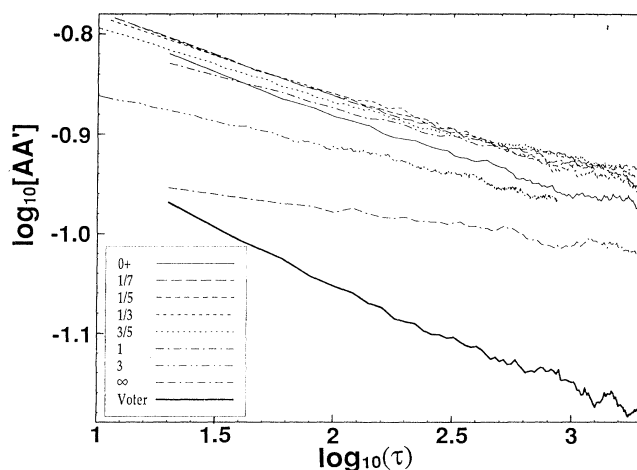


FIG. 1. Simulated poisoning kinetics for the monomer-monomer reaction model for various $k$ shown in the legend, and for the voter model. Plotted is the logarithm of the concentration of $AA'$ pairs vs $\log_{10}(\tau)$; slopes give the exponent $-\omega$.

TABLE I. Effective exponents describing poisoning kinetics for the voter model and for the monomer-monomer ($AB$) reaction model for various $k$.

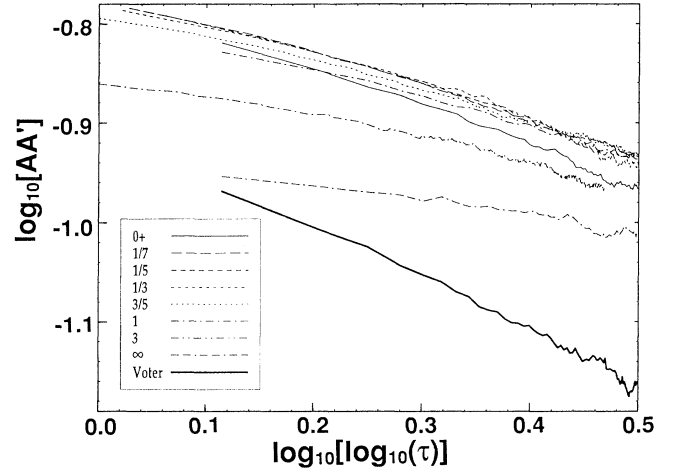| | $\dfrac{k}{1+k}$ | $\omega$ | $\sigma$ |
|---|---|---|---|
| Voter | $0^+$ | 0.096 | 0.59 |
| $AB\ k=0^+$ | $0^+$ | 0.078 | 0.51 |
| $AB\ k=\frac{1}{7}$ | $\frac{1}{8}$ | 0.071 | 0.38 |
| $AB\ k=\frac{1}{5}$ | $\frac{1}{6}$ | 0.083 | 0.47 |
| $AB\ k=\frac{1}{3}$ | $\frac{1}{4}$ | 0.083 | 0.46 |
| $AB\ k=\frac{3}{5}$ | $\frac{3}{8}$ | 0.070 | 0.33 |
| $AB\ k=1$ | $\frac{1}{2}$ | 0.052 | 0.32 |
| $AB\ k=3$ | $\frac{3}{4}$ | 0.058 | 0.31 |
| $AB\ k=\infty$ | 1 | 0.043 | 0.26 |



FIG. 2. Simulated poisoning kinetics for the monomer-monomer reaction model for various $k$ shown in the legend, and for the voter model. Plotted is the logarithm of the concentration of $AA'$ pairs vs $\log_{10}(\log_{10}(\tau))$; slopes give the exponent $-\sigma$.

monomer-monomer reaction (Table I) and $\sigma=0.59$ for the voter model.

Thus from these simulation studies it is reasonable to conclude that the monomer-monomer reaction model for various $k$ and the voter model exhibit fundamentally the same behavior. However, the precise form of the asymptotic decay is unclear. Fortunately, further elucidation is possible via analytic treatment for the $k=0^+$ monomer-monomer reaction and for the voter model. It is, of course, possible to write down an exact hierarchy of rate equations for various subconfiguration probabilities either directly [1] (accounting for all possible ways of creating and destroying the subconfiguration), or by first mapping the process onto a spin system [8,16]. The latter approach has been applied only to the $k=0^+$ monomer-monomer problem treating $A$'s ($B$'s) as spin $+1$ ($-1$), but it can also be applied to the voter model. Previous studies have focused on the case of equal adsorption rates, $p_A=p_B=\frac{1}{2}$. The key observation here was that the single-site probabilities satisfy a closed set of equations, as do the pair probabilities, except for coupling back to the single-site quantities [8,16]. In fact, $n$-point probabilities couple only to themselves and to $(n-1)$-point probabilities. Just as for the Glauber model [17], the randomly hopping lattice gas model [18], or the equilibrium single-step model [19], it is this feature that facilitates analytic treatment of the model.

We consider first the translationally invariant $k=0^+$ monomer-monomer reaction (without diffusion) on a square lattice, and directly develop a set of equations for

the probabilities of $A$-filled pairs of sites (cf. Ref. [1]). One finds that

$$\frac{d}{d\tau}[AA]=2p_A^2[AB]+2p_A\left\{[ABA]+2\begin{bmatrix}AB\\A\end{bmatrix}\right\}$$
$$-2p_B\left\{[AAB]+2\begin{bmatrix}AA\\B\end{bmatrix}\right\},\qquad(5)$$

where, as previously, square brackets indicate probabilities or "concentrations" of the configurations enclosed. Here the first two gain terms describe the transformation $AB\rightarrow AA$ for a specific pair of sites under consideration: in the first term, the $A$ and $B$ in the pair under consideration react and are replaced by deposition of two $A$'s; in the second term, the $B$ reacts with an $A$ other than the one in the pair under consideration, so deposition of just one $A$ is required to form an $AA$ pair on the pair of sites under consideration. The last loss term describes the transformation $AA\rightarrow AB$ for a specific pair of sites under consideration by reaction of the right $A$ with an adjacent $B$ and subsequent replacement by a $B$. The 2's are symmetry numbers. Similarly, for a separated pair of $A$'s one has

$$\frac{d}{d\tau}[A\text{---}A]=2p_A\left\{[A\text{---}AB]+\begin{bmatrix}A\\A\text{---}B\end{bmatrix}+[A\text{---}BA]+\begin{bmatrix}A\text{---}B\\A\end{bmatrix}\right\}$$
$$-2p_B\left\{[A\text{---}BA]+\begin{bmatrix}B\\A\text{---}A\end{bmatrix}+[A\text{---}AB]+\begin{bmatrix}A\text{---}A\\B\end{bmatrix}\right\}.\qquad(6)$$

Henceforth we consider only the case $p_A=p_B=\frac{1}{2}$, which facilitates fundamental reduction of (5) and (6). First it is necessary to use conservation of probability relationships to convert all configurations appearing in (5)

and (6) to ones which involve only $A$'s. Thus, for example, we use the identities $[AB]=[A]-[AA]$, $[ABA]=[A-A]-[AAA]$, $[AAB]=[AA]$ $-[AAA]$, $[A\text{---}AB]=[A\text{---}A]-[A\text{---}AA]$, etc. Sub-
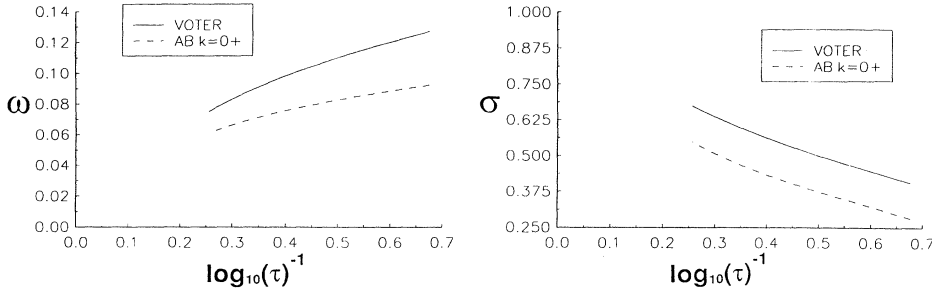
FIG. 3. Analytic estimates of the $\tau$ dependence of effective exponents $\omega(\tau)$ and $\sigma(\tau)$ describing poisoning kinetics. Results for both the $k=0^+$ monomer-monomer ($AB$) reaction model and the voter model are shown.

stitution into (5) and (6) shows that all three-site probabilities cancel out in the special case where $p_A = p_B$ (but in no other case). Before writing out the resulting equations, it is convenient to introduce a more compact notation. Thus we let $P_{ij}$ denote the concentration of pairs of $A$'s separated by $(i,j)$, so by symmetry $P_{i-j} = P_{ij}$ and $P_{-ij} = P_{ij}$. Let $\Delta$ denote the discrete Laplace operator $\Delta P_{ij} = P_{i+1j} + P_{ij+1} + P_{ij-1} + P_{i-1j} - 4P_{ij}$. Then after the above-mentioned cancellation for $p_A = p_B$, (5) and (6) become

$$\frac{d}{d\tau}P_{10} = P_{20} + P_{11} + P_{-11} - (3+\chi)P_{10} + \chi[A] ,$$

$$\frac{d}{d\tau}P_{ij} = \Delta P_{ij} \quad \text{for } |i|+|j| \geq 2 , \tag{7}$$

with $\chi = \frac{1}{2}$. These equations are consistent with Ref. [8], where the focus was on analysis of the increase of the total correlation, and subsequent estimation of the poisoning time for finite systems. Here instead we focus on the poisoning kinetics, and specifically the concentration $[AB]$ of adjacent $AB = AA'$ pairs, which gives the reaction rate. Thus we let $Q_{ij}$ denote the concentration of $AB$ pairs of separation $(i,j)$, i.e., $Q_{ij}$ gives the probability of finding an $A$ at $(0,0)$ and a $B$ at $(i,j)$. Then one has $Q_{ij} = [A] - P_{ij}$ and $Q_{10} = [AB]$. For an initially random distribution of $A$'s and $B$'s, from (7) it is easy to see that $Q_{ij} = [A](1-[A])S_{ij} = [B](1-[B])S_{ij}$, where the $S_{ij}$ are independent of $A$ and satisfy

$$\frac{d}{d\tau}S_{10} = S_{20} + S_{11} + S_{-11} - (3+\chi)S_{10} ,$$

$$\frac{d}{d\tau}S_{ij} = \Delta S_{ij} \quad \text{for } |i|+|j| \geq 2 . \tag{8}$$

The random initial condition corresponds to $S_{ij} = 1$, for all $i$ and $j$.

The above analysis can be repeated for the voter model. The key difference is that $p_A^2$ is replaced by $p_A$ in the first term of (5). Consequently, one finds that Eq. (8) still applies but with $\chi = 1$.

Numerical solution of these equations is possible after truncation, e.g., by setting $S_{ij} \equiv 1$, for $|i|$ and $|j|$ sufficiently large. [It is easy to check during integration of (8) that errors introduced by such truncation are insignificant over the time range considered; we truncate at $|i|$, $|j| > 350$ to determine $S_{ij}$ for $\tau < 8000$.] This allows determination of the behavior of $[AA'] = [AB] = [A](1-[A])S_{10}$ consistent with, but

more precise than, above simulation estimates. Results from integration of (8) for the effective exponents

$$\omega(\tau) = d \log_{10}([AB])/d \log_{10}(\tau)$$

and

$$\sigma(\tau) = d \log_{10}([AB])/d \log_{10}(\log_{10}(\tau))$$

are shown in Fig. 3 for both models. It appears that $\sigma(\tau)$ increases monotonically, approaching a value between 0.8 and 1, as $\tau \to \infty$ (a limit of unity is certainly consistent with our data), but this behavior is achieved very slowly. If $\sigma(\tau)$ approaches any finite value, as $\tau \to \infty$, then one must conclude that $\omega(\tau) \to 0$, as $\tau \to \infty$. This is also consistent with our data. It is also clear that it is practically impossible to determine the true asymptotic behavior of the poisoning kinetics via simulation. In Sec. IV, we show that for the one-dimensional versions of these models, rate equations analogous to (8) can be solved completely via standard techniques [18,20] to recover, e.g., the well-known result $[AA'] \sim \tau^{-1/2}$.

Finally we mention a relevant previous study. For the voter model, it has been shown [10,21] that the (probability distribution for the) side length $l$ of the largest square containing just one species, and including the origin, scales like $\log_{10}(\tau)$. One might then expect that $[AA']$ should scale like $\log_{10}(\tau)^{-1}$. However, if the growing clusters have an "active zone" with $O(1)$ defect density, the width of which scales like $l^\nu$, then $[AA']$ would scale like $\log_{10}(\tau)^{\nu-1}$. (See Ref. [22] for a discussion of similar issues applied to multi-Eden-cluster growth.) Thus our results for $\sigma(\tau)$ in Fig. 3 above can be used to extract values for an effective $\nu(\tau) = 1 - \sigma(\tau)$. Our data are consistent with the expectation that $\nu(\tau) \leq \frac{1}{2}$ for large clusters, and allow that $\nu(\tau)$ may vanish as $\tau \to \infty$.

## III. EPIDEMIC ANALYSIS

Here we present results of an "epidemic analysis" for the monomer-monomer reaction with $p_A = p_B = \frac{1}{2}$ and for the voter model (without diffusion). In such an analysis, the system is initially completely covered or poisoned by species $B$, say, except for a small patch. We determine the behavior of the "survival" probability $P_s$ that the system is not completely poisoned, as a function of time. This type of analysis is commonly used to determine the critical behavior of models with nonequilibrium phase transitions to adsorbing or poisoned states [5,11,12]. In such studies, right at the transition, one finds that
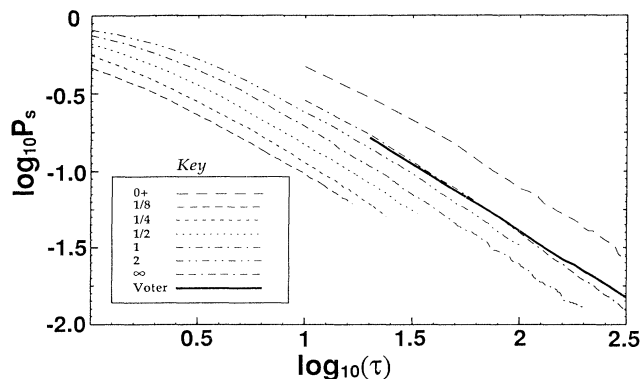
FIG. 4. Simulation results for the decay of the survival probability $P_s$ with reduced time $\tau$ for epidemic analyses of the monomer-monomer reaction model for various $k$ shown in the legend, and for the voter model. Slopes of these $\log_{10}(P_s)$ vs $\log_{10}(\tau)$ plots give the exponent $-\delta$.

$P_s \sim t^{-\delta}$, where $\delta$ is a nontrivial exponent and provides information on the universality class. For the voter model, however, if one exploits the connection with coalescing random walks [10,23], it follows that $P_s \sim \log_{10}(\tau)/\tau$, so one should find $\delta = 1$.

In our simulations, we somewhat arbitrarily start with a $B$-covered lattice except for an empty pair of sites for $k > 0$ monomer-monomer reaction models, or an $A$-filled pair if $k = 0^+$ and for the voter model. Results are obtained from $O(10^4)$ trials. Figure 4 shows our simulation results for $\log_{10}(P_s)$ vs $\log_{10}(\tau)$, and corresponding $\delta$ values are shown in Table II. These $\delta$ values are typically slightly below unity, but certainly consistent with a true asymptotic value of $\delta = 1$. (Any logarithmic correction of the form suggested above would produce lower effective values.) In Table II, we have also given slopes obtained from $\log_{10}(P_s)$ vs $\log_{10}(\tau/\log_{10}(\tau))$ for the $k = 0^+$ monomer-monomer reaction and voter model, and $\log_{10}(P_s)$ vs $\log_{10}(t/\log_{10}(t))$ for $k > 0$ monomer-monomer reaction models. These slopes are also con-

TABLE II. Effective exponents describing the decay of the survival probability $P_s$ for the voter model and for epidemic analyses of the monomer-monomer ($AB$) reaction model for various $k$. We have fit to $P_s \sim \tau^{-\delta}$, and $\log_{10}(P_s) \sim -\hat{\delta}\log_{10}(t/\log_{10}(t))$ for $k > 0$, or $\log_{10}(P_s) \sim -\hat{\delta}\log_{10}(\tau/\log_{10}(\tau))$ for $AB$ $k = 0^+$ and voter models.

| | $\dfrac{k}{1+k}$ | $\delta$ | $\hat{\delta}$ |
|---|---|---|---|
| Voter | $0^+$ | 0.891 | 1.08 |
| $AB$ $k = 0^+$ | $0^+$ | 0.899 | 1.09 |
| $AB$ $k = \frac{1}{8}$ | $\frac{1}{9}$ | 0.896 | 1.02 |
| $AB$ $k = \frac{1}{4}$ | $\frac{1}{5}$ | 0.903 | 1.12 |
| $AB$ $k = \frac{1}{2}$ | $\frac{1}{3}$ | 0.922 | 1.15 |
| $AB$ $k = 1$ | $\frac{1}{2}$ | 0.907 | 1.17 |
| $AB$ $k = 2$ | $\frac{2}{3}$ | 0.906 | 1.20 |
| $AB$ $k = \infty$ | 1 | 1.031 | 1.26 |

sistent with a true asymptotic value of $\delta = 1$. From these results, it is reasonable to assert that the monomer-monomer reaction model for various $k$, and the voter model, exhibit fundamentally the same behavior characterized by $\delta = 1$.

## IV. MODEL EXTENSIONS: DIFFUSION

It should be noted that various natural extensions of these monomer-monomer reaction models (with $p_A = p_B$) might be considered. If one introduces desorption in a finite system of $N$ sites, one observes a transition from bistability to monostability as the desorption rate increases above $O(N^{-1})$. This has been demonstrated analytically for infinitesimal reaction rates using appropriate rate equations of the form (5)–(8) or the corresponding spin representation [8,16,26].

One can also introduce diffusion, the randomizing effect of which works against the clustering propensity of the reaction. This competition has been studied to date only for one case of finite reaction rate [27]. Here we consider the $k = 0^+$ monomer-monomer ($AB$) reaction and the voter model with diffusion corresponding to random $A$-$B$ place exchange at rate $h = h_{AB}$ or $h_v$ (on a time scale $\tau$), respectively. Recall that here the surface is completely covered with $A$ and $B$. Again analytic treatment is possible by simply augmenting (7) or (8) with the appropriate random hopping terms. See Ref. [18] for a detailed discussion of these terms. Specifically, one adds a term $2h(S_{20} + S_{11} + S_{-11} - 3S_{10})$ to $(d/d\tau)S_{10}$, and $2h\Delta S_{ij}$ to $(d/d\tau)S_{ij}$ for $|i| + |j| \geq 2$. Setting $\tau' = (1 + 2h)\tau$ and $\varepsilon = \chi/(1 + 2h)$ (so $0 < \varepsilon \leq \frac{1}{2}$ for the $k = 0^+$ $AB$ model, and $0 < \varepsilon \leq 1$ for the voter model), one obtains

$$\frac{d}{d\tau'}S_{10} = (S_{20} + S_{11} + S_{-11} - 3S_{10}) - \varepsilon S_{10} \ ,$$

$$\frac{d}{d\tau'}S_{ij} = \Delta S_{ij} \quad \text{for } |i| + |j| \geq 2 \ . \tag{9}$$

It thus becomes apparent from (9) that the $k = 0^+$ $AB$ model with $h_{AB} \geq 0$ is equivalent to the voter model with $h_v = \frac{1}{2}(1 + 4h_{AB}) \geq \frac{1}{2}$ at the level of the pair probabilities (after a simple rescaling of time). The same equivalence is also found for $n$-point probabilities with $n \geq 3$. In particular, the $k = 0^+$ $AB$ model with no diffusion is equivalent to the voter model with $h_v = \frac{1}{2}$.

This last result can be rationalized directly by considering the possible transitions from an $AB$ pair of sites. For the diffusionless $k = 0^+$ $AB$ model, it is clear that the state of these sites can change to one of $AA$, $BA$, or $BB$ with equal probabilities of $\frac{1}{4}$ (or remain as $AB$ with probability $\frac{1}{4}$). This is not the case for the diffusionless voter model where $AB$ changes to either $AA$ or $BB$ with equal probability. However, introducing exchange diffusion at rate $h_v = \frac{1}{2}$ in the voter model guarantees that one of $AA$, $BA$, or $BB$ is again chosen with equal probability.

The evolution equations (9), which are of the same form as (8), have a simple interpretation in terms of random walks. Consider a particle undergoing a random walk between neighboring sites $(i,j) \neq (0,0)$ on a square

lattice with a hop rate of unity, and with the additional possibility of irreversible adsorption at (0,0) from neighboring sites with "small" rate $\varepsilon$. Then $S_{ij}$ represents the probability of finding the particle at site $(i,j)$. The recurrence property for two-dimensional random walks suggests that even for our unnormalized initial conditions, one will find that $S_{ij} \to 0$, as $\tau' \to \infty$, no matter how small $\varepsilon$. Thus we conclude that for any $h > 0$, the process still poisons, i.e., there is no reactive steady state. Figure 5 shows numerical evidence to support this claim. Specifically, the effective exponent

$$\sigma(\tau') = d \, \log_{10}([\,AB\,])/d \, \log_{10}(\log_{10}(\tau'))$$

is shown to increase monotonically as $\tau' \to \infty$, for various $h \geq 0$, leading to the conclusion that $\sigma(\infty) > 0$, which confirms that poisoning must occur.

Finally, it is instructive to consider the one-dimensional versions of these $k = 0^+$ monomer-monomer reaction and voter models with diffusion. Let $Q_i = [A](1-[A])S_i$ denote the concentration of $AB$ pairs of separation $i$. (Thus $Q_i$ gives the probability of finding an $A$ at the origin, and a $B$ at site $i$.) Then it is easy to show that (9) is replaced by

$$\frac{d}{d\tau'}S_1 = (S_2 - S_1) - \varepsilon S_1 \ , \quad \frac{d}{d\tau'}S_i = \Delta S_i \quad \text{for } i \geq 2 \ , \quad (10)$$

where $\tau'$ and $\varepsilon$ are exactly as above, but now $\Delta S_i = S_{i+1} - 2S_i + S_{i-1}$. The random initial condition corresponds to $S_i = 1$ for all $i$. From a spectral decomposition [20] of the evolution operator associated with (10), together with appropriate treatment of the unnormalized initial conditions [18], we obtain the solution

$$S_i(\tau') = \pi^{-1} \int_0^{\pi} d\phi \exp[-4\sin(\tfrac{1}{2}\phi)^2 \tau']$$

$$\times \sin(i\phi + \eta)\cos(\tfrac{1}{2}\phi + \eta)/\sin(\tfrac{1}{2}\phi) \ . \quad (11)$$

Here the real-valued "phase shift" $\eta = \eta(\phi)$ satisfies

$$e^{2i\eta} = [1 + (\varepsilon - 1)e^{-i\phi}]/[1 + (\varepsilon - 1)e^{i\phi}] \ .$$

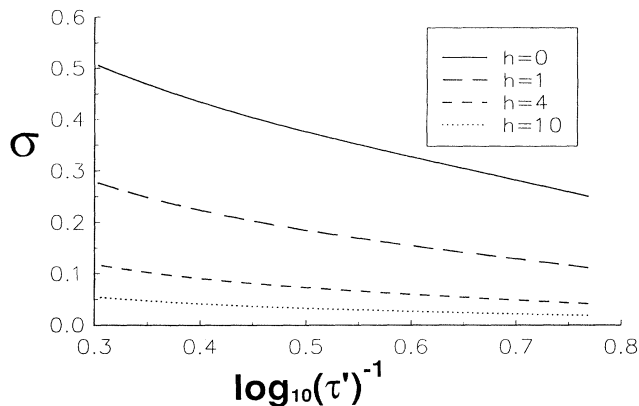Note that the diffusionless voter model corresponds to



FIG. 5. Analytic estimates of the $\tau'$ dependence of the effective exponent $\sigma(\tau')$ describing the poisoning kinetics of the $k = 0^+$ $AB$ model with place-exchange diffusion for various rates $h \geq 0$, shown.

the particularly simple case where $\varepsilon = 1$, so $\eta \equiv 0$. An asymptotic analysis of (11) yields

$$S_i \sim \pi^{-1/2}[i + (1 - \varepsilon)\varepsilon^{-1}]/(\tau')^{1/2} \quad \text{as } \tau' \to \infty \ . \quad (12)$$

Thus the reaction rate, which is determined by $[AB] = [A](1 - [A])S_1$, always vanishes like $(\tau')^{-1/2}$, and like $\varepsilon^{-1}(\tau')^{-1/2}$ in the regime of large diffusion rates $h$ or small $\varepsilon = \chi/(1 + 2h)$.

## V. CONNECTION WITH THE MONOMER-DIMER REACTION

We now briefly comment on certain aspects of the behavior of the monomer-dimer surface reaction

$$A(g) + * \to A(ad) \ , \quad B_2(g) + 2* \to 2B(ad) \ ,$$
$$A(ad) + B(ad) \to AB(g) + 2* \ . \quad (13)$$
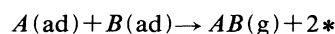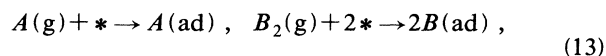
on a square lattice. Again, adsorption rates $p_A$ and $p_B$ for $A$ and $B$ satisfy $p_A + p_B = 1$, and $k$ denotes the reaction rate. Adsorbed species are immobile. Thus one obtains the rate equations

$$\frac{d[A]}{dt} = p_A[E] - 4k[AB] \ ,$$
$$\frac{d[B]}{dt} = 2p_B[EE] - 4k[AB] \ . \quad (14)$$

For $k > 0$, the distribution of adsorbed species can potentially adjust to achieve a nontrivial steady state for a finite range of $p_1 \leq p_A \leq p_2$. In this steady state, one has $p_A[E] = 2p_B[EE]$. On the other hand, for $k = 0^+$, this process reduces to the voter model for $p_A = \frac{1}{5}$ [1,5,14]: once an $AB$ pair reacts, the empty pair formed is immediately filled by two $B$'s via $B_2$ deposition, or sequentially by two $A$'s. (This is precisely the same behavior as in the above-mentioned dimer-dimer reaction.) One can show [5,14,15] that equal effective adsorption rates for $A$ and $B$ corresponds to $p_A = \frac{1}{5}$; for $p_A > \frac{1}{5}$ ($p_A < \frac{1}{5}$), the system "quickly" poisons with $A$ ($B$). Thus the range $\delta p_A = p_2 - p_1$ supporting a reactive steady state must clearly shrink to zero as $k \to 0+$ ($p_1 = p_2 = \frac{1}{5}$ and $\delta p_A = 0$ at $k = 0^+$, compared with $p_1 = 0.390$, $p_2 = 0.525$, and $\delta p_A = 0.135$ at $k = \infty$ [24]). An interesting conjecture has been made [14,25] suggesting that $\delta p_A \equiv 0$ for $0 \leq k \leq k_c$, where the tricritical point is located at $k_c \approx 0.08$. This claim, which has been disputed recently [15], is reconsidered here.

Suppose that $k_c > 0$. One might expect that for $k < k_c$ when $p_A = p_1 = p_2$, since any slight perturbation of the relative adsorption rates would cause rapid poisoning, the system should exhibit voter or monomer-monomer reaction-model-type behavior. If this is true, then an epidemic analysis for an empty patch in an $A$-poisoned background at $p_A = p_2$ should yield the voter model value of $\delta = 1$, in contrast to the much higher values found previously [5] for the monomer-dimer reaction with $k \geq \frac{1}{10}$. We have performed such an analysis for $k = \frac{1}{20}$ (well below the predicted value of $k_c$ above) at the appropriate $p_2 \approx 0.2576$. [This $p_2$ value was determined by varying
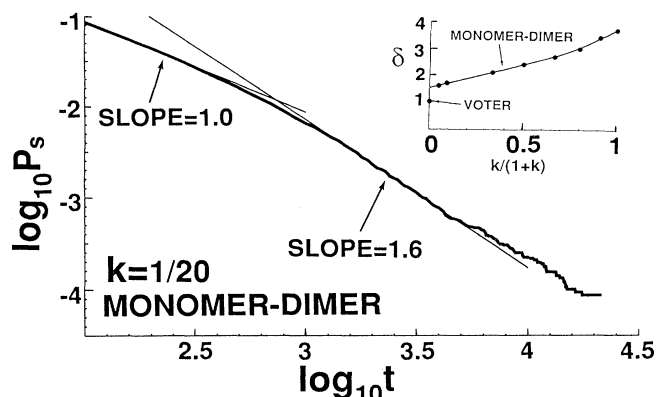
FIG. 6. Simulation results for the decay of the survival prob-ability $P_s$ starting with a $2 \times 1$ empty patch in an $A$-poisoned background for the monomer-dimer $(AB_2)$ reaction model with $k = \frac{1}{20}$ and $p_A = p_2 \approx 0.2576$. The slope of $\log_{10}(P_s)$ vs $\log_{10}(t)$ gives $-\delta$. The inset shows the variation of $\delta$ with $k$ for the monomer-dimer model, as compared with $\delta$ for the voter model.

$p_A$ until $\log_{10}(P_s)$ was found to decay asymptotically linearly with $\log_{10}(t)$; $\log_{10}(P_s)$ saturates for $p_A < p_2$, and decreases faster than linearly for $p_A > p_2$.] One finds a distinct crossover from voter model behavior with $\delta \approx 1.0$ for shorter times to "finite-$k$" behavior with $\delta \approx 1.6$ for larger times (Fig. 6). This suggests that there is no tricrit-ical point $k_c > 0$ (or at least that $k_c < \frac{1}{20}$). This analysis relies on the surprising observation that for the monomer-dimer model with $k > 0$, $\lim_{k \to 0} \delta(k) \approx 1.5$ differs from the voter model value of $\delta = 1$.

## VI. CONCLUSIONS

In this study, we have shown that the behavior of the diffusionless monomer-monomer surface reaction model,

with equal reactant adsorption rates and various reaction rates, is fundamentally the same as that of the voter mod-el. We also conclude from analytic calculations that the slow poisoning kinetics exhibited by the $k = 0^+$ monomer-monomer reaction and the voter model is most appropriately described by the form $[AA'] \sim \log_{10}(\tau)^{-\sigma}$, with $\sigma$ close to (and possibly equal to) unity. We em-phasize that it is practically impossible to determine this true asymptotic behavior from simulations. Introduction of place-exchange diffusion to the $k = 0^+$ monomer-monomer reaction and voter models does not change their basic poisoning behavior. It does, however, eluci-date the relationship between them. In this contribution, it is also shown that the survival probability in an "epi-demic analysis" of the diffusionless monomer-monomer reaction model decays like $P_s \sim \tau^{-1}$, with possible loga-rithmic corrections, again consistent with voter model behavior. Our understanding of the monomer-monomer reaction and voter models is useful for elucidating the be-havior of the monomer-dimer reaction model with low reaction rate, and can also be applied to elucidate the be-havior of a simplistic $A + BC$ model for the CO+NO re-action [28].

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