Exact results for kinetics of catalytic reactions

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The kinetics of an irreversible catalytic reaction on a substrate of arbitrary dimension is examined. In the limit of infinitesimal reaction rate (reaction-controlled limit), we solve the dimer-dimer surface reaction model (or voter model) exactly in arbitrary dimension D. The density of reactive interfaces is found to exhibit a power-law decay for $D < 2$ and a slow logarithmic decay in two dimensions. We discuss the relevance of these results for the monomer-monomer surface reaction model.

In modeling heterogeneous catalysis [1], the monomer-monomer surface reaction model plays an important role, at least from the theoretical point of view since an appealing simplicity of this model allows one to examine several issues analytically. In particular, investigations of the monomer-monomer model clarified the role of fluctuations [2–8], interfacial roughening [9], diffusion of the adsorbants [10], and surface disorder [11]. In the simplest situation (no diffusion, no disorder, etc.), it was found that single-species clusters grow with time when the dimensionality D of the substrate is sufficiently small, $D \leq 2$. However, the details of the coarsening like the decay rate of the density of reactive interfaces remain uncertain in two dimensions — simulations [5,12,13] revealed a very slow decay which could be logarithmic or power law with a small exponent. In this paper, we clarify these questions by computing analytically kinetic characteristics of an idealized version of the monomer-monomer model, the *voter model*. We then expand these results and perform numerical simulations for the full model.

The monomer-monomer surface reaction process can be schematically represented by the following kinetic steps:

$$A + V \xrightarrow{k_A} A_V,$$

$$B + V \xrightarrow{k_B} B_V, \qquad (1)$$

$$A_V + B_V \xrightarrow{k_r} AB\uparrow + 2V.$$
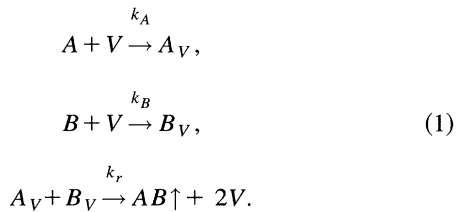
A and B particles impinge upon a surface, with respective rates k_A and k_B, and adsorb onto vacant sites V to form a monolayer of adsorbed particles, A_V and B_V. Nearest-neighbor pairs of dissimilar adsorbed particles, $A_V B_V$, react and desorb with rate k_r, leaving behind two vacancies. For $k_A \neq k_B$, the adsorption imbalance leads to the quick saturation of the surface by the majority species. For $k_A = k_B$ and for dimensions $D \leq 2$, there is a fluctuation-induced coarsening of the surface into growing A and B adsorbed islands. This nontrivial case of equal adsorption rates will be considered in the following. Furthermore, in theoretical analysis we will restrict ourselves to the *reaction-controlled* limit, $k_r \ll k_A = k_B$, which was found to provide qualitatively the same behavior as the general case [4,6] but more amenable to theoretical treatment.

In the reaction-controlled limit, the substrate quickly becomes completely covered and then stays covered forever, since in units of the typical, i.e., adsorption, time interval unoccupied sites are refilled instantaneously. The kinetics of the monomer-monomer surface reaction model is conveniently described by a mapping onto the Ising model with mixed zero-temperature voter dynamics and infinite-temperature Kawasaki dynamics [8]. Remember that in the voter model [14], sites have two opinions which can be marked by A and B. Each site keeps its opinion some time interval, distributed exponentially with characteristic time τ, and then assumes an opinion of a randomly chosen neighboring site. If a site is surrounding by similar sites it does not change its opinion and therefore the voter dynamics is zero-temperature in nature. In the original monomer-monomer model, the reacting neighboring sites, A_V and B_V, desorb and then unoccupied sites immediately refilled by $A_V B_V$ (no reaction), $A_V A_V$ or $B_V B_V$ (voter dynamics), or $B_V A_V$ (Kawasaki exchange dynamics whose effective temperature is infinite since the reaction rate does not depend on the content of neighboring sites). Thus the voter model can be considered as an idealized variant of the monomer-monomer model.

Interestingly, the voter model can be *exactly* mapped onto the reaction-controlled limit of the dimer-dimer surface reaction model [13]. Indeed, in the dimer-dimer model an empty pair that appears after the reaction event, $A_V + B_V \rightarrow AB\uparrow + 2V$, is refilled by an A_2 or a B_2 dimer, so the resulting dynamics is identical to the voter model dynamics. However, natural initial states for the voter model and the dimer-dimer surface reaction model are different. For the voter model, a lattice completely covered by A and B monomers without correlations in initial positions provides a reasonable initial condition. For the dimer-dimer model, if we start from an empty lattice and fill it by random sequential adsorption of dimers one cannot reach a fully covered lattice and instead approach a so-called jammed state with some single-site vacancies [15]; this jammed state provides natural initial condition for the dimer-dimer model. In the following, we will consider only completely covered initial states.

A remarkable feature of the voter model is its solvability. It is evident in one dimension where the voter model is identical to the kinetic Ising model with zero-temperature Glauber dynamics [14,16]. Surprisingly, the voter model can be solved in arbitrary dimension and thus appears to be one

of a very few models which are solvable in any D. Moreover, the voter model can be solved on an arbitrary lattice although for simplicity we will focus on a (hyper)cubic lattice. To reveal the solvability of the voter model, the spin formulation is convenient. Identifying A's (B's) with $+$ ($-$) spins so that the state of the substrate is described by $S \equiv [S_\mathbf{k}]$, $\mathbf{k} = (k_1, \ldots, k_D)$, one can verify that the spin-flip rate, $W_\mathbf{k}(S) \equiv W(S_\mathbf{k} \rightarrow -S_\mathbf{k})$, reads

$$W_\mathbf{k}(S) = \frac{1}{\tau} \left(1 - \frac{1}{2D} S_\mathbf{k} \sum_{\mathbf{e}_i} S_{\mathbf{k}+\mathbf{e}_i} \right). \quad (2)$$

Here the sum in the right-hand side runs over all $2D$ nearest neighbors and τ defines the time scale of the process. In the following, we will set $\tau = 4/D$ to simplify numerical factors in equations for correlators. The probability distribution $P(S,t)$ satisfies the master equation

$$\frac{d}{dt} P(S,t) = \sum_\mathbf{k} [W_\mathbf{k}(S^\mathbf{k})P(S^\mathbf{k},t) - W_\mathbf{k}(S)P(S,t)], \quad (3)$$

where the state $S^\mathbf{k}$ differs from S only at the site $\mathbf{k}$. One can then derive a set of differential equations for the spin correlation functions $\langle S_\mathbf{k} \cdots S_\mathbf{l} \rangle \equiv \Sigma_S S_\mathbf{k} \cdots S_\mathbf{l} P(S,t)$. For the single-body correlation functions we get [8]

$$4\frac{d}{dt} \langle S_\mathbf{k} \rangle = \Delta_\mathbf{k} \langle S_\mathbf{k} \rangle. \quad (4)$$

Here $\Delta_\mathbf{k}$ denotes a difference Laplace operator,

$$\Delta_\mathbf{k} \langle S_\mathbf{k} \rangle = -2D\langle S_\mathbf{k} \rangle + \sum_{\mathbf{e}_i} \langle S_{\mathbf{k}+\mathbf{e}_i} \rangle. \quad (5)$$

For the two-body correlation functions one has [8]

$$4\frac{d}{dt} \langle S_\mathbf{k} S_\mathbf{l} \rangle = (\Delta_\mathbf{k} + \Delta_\mathbf{l}) \langle S_\mathbf{k} S_\mathbf{l} \rangle. \quad (6)$$

Similar equations can be written for higher-body correlation functions. An important feature of these equations which allows an analytical treatment is their recursive nature — to solve for an n-body correlation function one does not need the higher correlation functions. The structure of equations for correlators is similar to the one that arises in the one-dimensional kinetic Ising model with zero-temperature Glauber dynamics [16] which is equivalent to the voter model in one dimension (1D).

The general solution to Eq. (4) reads

$$\langle S_\mathbf{k} \rangle = e^{-Dt/2} \sum_\mathbf{l} \sigma_\mathbf{l} I_{\mathbf{k}-\mathbf{l}}(t/2). \quad (7)$$

Here $I_\mathbf{k}(x)$ is the shorthand notation for the multi-index Bessel function, $I_\mathbf{k}(x) = \Pi_{1 \leq j \leq D} I_{k_j}(x)$, with I_n being the usual modified Bessel function, and $\sigma_\mathbf{l} = \langle S_\mathbf{l} \rangle (t=0)$.

Although the evolution rules of the voter model do not preserve locally the densities of A's and B's, Eq. (7) shows that $\Sigma_\mathbf{k} \langle S_\mathbf{k} \rangle = \Sigma_\mathbf{l} \sigma_\mathbf{l}$, the total densities are conserved. Note, however, that for any *finite* substrate intuitively more appealing behavior emerges: The effect of fluctuations leads to saturation, i.e., all voters eventually share the same opinion thereby stopping the dynamics.

To find the two-body correlation functions, we first make a simplifying assumption that the initial state is translationally invariant. Then $\langle S_\mathbf{k} S_\mathbf{l} \rangle$ will depend only on $\mathbf{m} = \mathbf{k} - \mathbf{l}$ for $t = 0$. Clearly, this holds for later times, too. In this situation, the shorthand notation $R_\mathbf{m} = \langle S_\mathbf{k} S_\mathbf{l} \rangle$ will be used. Thus for the translationally invariant initial conditions, Eq. (6) simplifies to the lattice diffusion equation

$$2\frac{d}{dt} R_\mathbf{m} = \Delta_\mathbf{m} R_\mathbf{m}, \quad (8)$$

which should be solved subject to the boundary condition $R_0(t) = 1$, since $R_0 = \langle S_\mathbf{k}^2 \rangle \equiv 1$. It is natural to choose an uncorrelated initial state, $R_\mathbf{m}(0) = 0$, for all $\mathbf{m} \neq \mathbf{0}$. Equation (8) is identical to Eq. (4) up to a numerical factor. Therefore, if we forget for a moment about the boundary condition, we can use Eq. (7) to get $\tilde{R}_\mathbf{m} = e^{-Dt} I_\mathbf{m}(t)$. However, $\tilde{R}_0 = [e^{-t} I_0(t)]^D$ disagrees with the boundary condition. To remove this discrepancy it is useful to consider the initial-value problem as the problem with a localized constant source at the origin and therefore to look for the solution of the form

$$R_\mathbf{m} = e^{-Dt} I_\mathbf{m}(t) + \int_0^t d\tau \, J_D(t-\tau) e^{-D\tau} I_\mathbf{m}(\tau). \quad (9)$$

Mathematically, Eq. (9) is a linear combination of exact solutions to Eq. (8) and therefore (9) also solves the linear Eq. (8). Physically, Eq. (8) corresponds to the case of initial source $R_0|_{t=0} = 1$ at the origin, supplemented by an additional input $J_D(\tau)d\tau$ which is added into the origin during the time interval $(\tau, \tau + d\tau)$ to keep the overall density at the origin unchanged, $R_0(t) \equiv 1$. Thus the input strength J_D obeys

$$1 - [e^{-t} I_0(t)]^D = \int_0^t d\tau \, J_D(t-\tau) [e^{-\tau} I_0(\tau)]^D. \quad (10)$$

The Laplace transform of the input strength, $\hat{J}_D(\lambda) = \int_0^\infty dt \, e^{-\lambda t} J_D(t)$, can be expressed through the Laplace transform $\hat{T}_D(\lambda)$ of the function $T_D(t) = [e^{-t} I_0(t)]^D$,

$$\hat{J}_D(\lambda) = -1 + \frac{1}{\lambda \hat{T}_D(\lambda)}. \quad (11)$$

Making use of the integral representation [17],

$$I_0(t) = \frac{1}{2\pi} \int_0^{2\pi} dq \, e^{t \cos q}, \quad (12)$$

we express $\hat{T}_D(\lambda)$ through the so-called Watson integrals,

$$\hat{T}_D(\lambda) = \int_0^{2\pi} \frac{d^D \mathbf{q}}{(2\pi)^D} \frac{1}{\lambda + D - \Sigma_{1 \leq j \leq D} \cos q_j}. \quad (13)$$

Combining these finding yields

$$\hat{J}_1(\lambda) = \left(\frac{\lambda + 2}{\lambda} \right)^{1/2} \quad (14)$$

in 1D and

$$\hat{J}_2(\lambda) = -1 + \pi \frac{\lambda+2}{2\lambda} K^{-1}\left(\frac{2}{\lambda+2}\right) \qquad (15)$$

in 2D. In Eq. (15), $K(x)$ is the complete elliptic integral of the first kind, $K(x) = \int_0^{\pi/2} d\theta (1-x^2 \sin^2\theta)^{-1/2}$. The final expressions for $J_D(t)$ are given by the inverse Laplace transform.

From the two-body correlation functions, physically interesting quantities can be found. One such quantity, the concentration $C_{AB}(t)$ of reactive interfaces, or nearest-neighbor adsorbed AB pairs, is given by $C_{AB} = (1-R_{e_i})/2$. A straightforward computation gives

$$C_{AB}(t) = \frac{1}{2} e^{-Dt} I_0^{D-1}(t)[I_0(t)-I_1(t)]$$
$$+ \frac{1}{2}\int_0^t d\tau\, J_D(t-\tau) e^{-D\tau} I_0^{D-1}(\tau)[I_0(\tau)-I_1(\tau)].$$
$$(16)$$

The long-time behavior is obtained by analyzing the low-λ limit. From Eqs. (13) and (11) we get

$$\hat{J}_D(\lambda) \sim \begin{cases} \lambda^{-D/2}, & D<2 \\ \lambda^{-1}\ln^{-1}(1/\lambda), & D=2 \quad \lambda\to 0 \\ \lambda^{-1}, & D>2 \end{cases} \qquad (17)$$

which imply

$$J_D(t) \sim \begin{cases} t^{-1+D/2}, & D<2 \\ (\ln t)^{-1}, & D=2 \quad t\to\infty \\ 1, & D>2. \end{cases} \qquad (18)$$

Combining Eqs. (16) and (18), and the asymptotic relations $I_0(t) \simeq I_1(t) \simeq e^t/\sqrt{2\pi t}$, the asymptotic behavior for the concentration of reactive interfaces

$$C_{AB}(t) \sim \begin{cases} t^{-1+D/2}, & D<2 \\ (\ln t)^{-1}, & D=2 \quad t\to\infty \\ a-bt^{-D/2}, & D>2. \end{cases} \qquad (19)$$

Thus in the long-time limit $C_{AB}\to 0$ when $D\leq 2$, i.e., the coarsening, takes place for low-dimensional substrates while for $D>2$ single-species domains do not arise.

In the borderline two-dimensional case the coarsening occurs but the concentration of reactive interfaces decreases very slowly. In the recent work [13], the decay of $C_{AB}(t)$ in the voter model has been studied numerically. Fitting data by power-law and logarithmic forms, $C_{AB}\sim t^{-\omega}$ and $C_{AB}\sim [\ln t]^{-\sigma}$, respectively, the effective exponents $\omega\approx 0.096$ and $\sigma\approx 0.59$ have been observed. The theoretical asymptotic value $C_{AB}(t)$ computed from Eq. (16) is

$$C_{AB}(t) = \frac{\pi}{2\,\ln(t)+\ln(256)} + O\left(\frac{\ln t}{t}\right) \qquad (20)$$
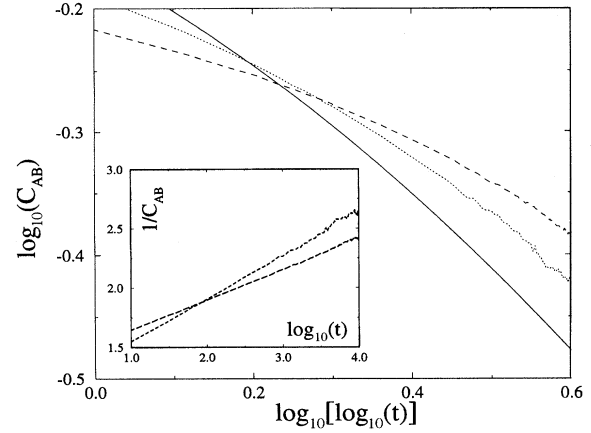

FIG. 1. The concentrations of interfaces $C_{AB}(t)$ as a function of time in a $\log_{10}$-$\log_{10}$($\log_{10}$) scale for the voter model (solid line), the monomer-monomer model in the reaction-controlled limit (dotted line), and in the adsorption-controlled limit (dashed line). The curvatures show that the true asymptotic regime is not reached. The insert show $1/C_{AB}$ as a function of $\log_{10}(t)$ for the last two cases. Straight lines are evidences for $\sigma=1$.

and therefore the asymptotic state arises on a very late stage which has not been reached in simulations [5,12,13]. In [13], Evans and Ray did simulations for times $t\leq 1500\tau$. However, trying to fit the exact result (20) with $C_{AB}\sim[\ln t]^{-\sigma}$, one can get at the very best the value $\sigma=0.72$ when $t\approx 1500\tau$.

Turn now to the monomer-monomer surface reaction model in the reaction-controlled limit. The voter model solution of Eq. (7) is still valid for the monomer-monomer model since addition of the infinite-temperature Kawasaki dynamics to the voter model dynamics just results in a change of time scale τ to $\tau/2$ in Eq. (4) [8]. Equation (6) for $|\mathbf{k-l}|>1$ also maintains its form, up to the replacement τ by $\tau/2$, while for $|\mathbf{k-l}|=1$, Eq. (6) undergoes more significant change [8]. However, in the long-time limit the growth of the characteristic space scale makes the underline lattice structure less and less important and hence the difference with the voter model behavior should decrease with time. So one can expect that the main difference between the concentration $C_{AB}(t)$ of the voter model and the monomer-monomer model lies in the time scale difference. This suggests that the asymptotic state for the monomer-monomer model is established later than for the voter model giving rise to a smaller effective exponent σ. This hypothesis is comforted by our simulations where, for longer times than in previous simulations [5,12,13], we have always found an effective exponent σ closer to unity (see Fig. 1).

We performed numerical simulations for the monomer-monomer model in the reaction-controlled limit on a square lattice of size $10^3\times 10^3$ in time interval $t\leq 10^4\tau$ for 25 samples. Both the size of the system and time span of the simulations were significantly bigger than in previous studies [5,12,13]. We found $\sigma\approx 0.67$ which is to be compared with $\sigma\approx 0.51$ for times $t\leq 1500\tau$ [13]. We believe that in a truly asymptotic regime the value $\sigma=1$ will appear. Moreover, we think that our results for the kinetics of the monomer-

monomer model of catalysis in the reaction-controlled limit are qualitatively valid for arbitrary reaction rates. In particular, for the opposite extreme, i.e., for the *adsorption-controlled* limit $(k_A = k_B \ll k_r)$, we have observed $\sigma \approx 0.49$ instead of $\sigma \approx 0.33$ [5] and $\sigma \approx 0.26$ [13]. Large time simulations are again closer to the true asymptotic regime where we think $(\ln t)^{-1}$ behavior should be recovered. For both cases, the curvatures of the lines in a $\log_{10}$-$\log_{10}(\log_{10})$ scale (see Fig. 1) show that the true asymptotic regime is not yet reached. Our belief in $C_{AB} \simeq 1/\log_{10}(at)$ where $\sigma = 1$ is comforted by the straight lines shown in the inset for $1/C_{AB}$ as a function of $\log_{10}(t)$.

In summary, for the voter model in arbitrary dimension we have found the exact expression for the two-body correlation functions. In the most interesting two-dimensional case our exact solution reveals, on the language of the catalysis model, that the density of reactive interfaces exhibits inverse logarithmic decay. It would be very interesting to find exact solutions for higher-body correlators. Given the fact that the one-dimensional voter model is *completely* solvable [18], exact results for low-body correlators in arbitrary dimension can indicate the complete solvability of the voter model for any D. Another direction of further research is to consider the dimer-dimer model of catalysis in the adsorption-controlled limit. Contrary to the monomer-monomer model, where there is some evidence that the qualitative behavior of the system is the same in the reaction- and adsorption-controlled limit, the behavior of the dimer-dimer model should be very different in these two limiting cases. In the adsorption-controlled limit, an infinite number of adsorbing states can play a significant role in the dynamics (existence of adsorbing states is evident, e.g., in one dimension any state with A- and B-islands separated by single empty sites will be an adsorbing state). Note that there are just two trivial adsorbing states for the monomer-monomer and monomer-dimer models so the dimer-dimer model is very different from these previously studied models. Rich kinetic behaviors, resembling those of the deposition-evaporation models [19,20], can be envisioned.

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