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Kinetics of catalytic reactions with diffusional relaxation

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The kinetics of an irreversible monomer-monomer model of heterogeneous catalysis is investigated. In this model, two reactive species, A and B, adsorb onto a catalytic substrate with a rate I and diffuse onto it with a diffusion rate D. Atoms of similar species aggregate to form immobile islands while atoms of dissimilar species combine and desorb from the substrate. In the limit of low coverage we find that the island-size distribution function exhibits a scaling behavior. In particular, a mean-field rate equation analysis shows that the density of the overall number of islands $N(t)$ and the average number of atoms per islands $S(t)$ follow power law behaviors: $N\sim(I^3t/D^2)^{1/5}$ and $S\sim(DIt^2)^{1/5}$. For the two-dimensional substrate we derive logarithmic corrections to the mean-field predictions, while in one dimension we develop a modified rate-equation approach that gives $N\sim(I^3t/D^2)^{1/7}$ and $S\sim(DI^2t^3)^{1/7}$.

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I. INTRODUCTION

Heterogeneous catalysis is a fundamental kinetic process in which the rate of chemical reactions is enhanced near a surface [1]. The classical example is oxidation, the process that does not readily occur in the gas phase but proceeds much faster when the species are adsorbed onto a catalytic substrate. The classical description of the kinetics of heterogeneous catalysis, the Langmuir theory [1], assumes that the reaction rate is a simple function of average densities of reactants and thus ignores all microscopic details. Recent theoretical approaches [2–11] consider various microscopic effects and, in particular, clarify the role of fluctuations.

In this paper, we investigate the kinetics of the *monomer-monomer* catalytic reaction. In this model, two different reactive species, A and B, adsorb onto the single sites of a catalytic substrate and nearest-neighbor AB pairs desorb from the substrate. Much of the previous work has assumed that the adsorbate remains immobile [6–11] although in a few recent studies the influence of surface diffusion has been tested numerically [12,13]. The diffusion of monomers clearly becomes important if the adsorption rates for both species are small enough. Moreover, even in the opposite limit of relatively large adsorption rates, the role of diffusion increases at least in the late stage of the catalysis process when the fraction of vacant sites decays, thus decreasing the efficiency of deposition.

We shall investigate the simplest monomer-momomer catalysis model, which incorporates (i) the adsorption of reactants onto the substrate, (ii) the diffusion of single atoms, (iii) the formation of immobile islands composed of more than one atom of a single species, and (iv) the desorption of nearest-neighbor pairs of atoms of dissimilar species. We shall assume that the escape of an atom from an island is forbidden. We shall examine a low-coverage regime in which coalescence of islands may be ignored. If nearest-neighbor pairs of similar atoms are immediately combined to form islands and nearest-neighbor pairs of dissimilar atoms are instantaneously desorbed, the catalysis process is *diffusion controlled.* In the opposite *reaction-controlled* case, the microscopic reaction rates are small compared to the rate of collisions, hence the mixing is perfect and one can expect the mean-field predictions to hold independently on the dimensionality of the substrate.

In the next section, we investigate the model without deposition. Although this case is not particularly useful in applications to catalysis, it may be interesting in other realizations of our model. We use the rate-equation approach and establish a surprising equivalence of the rate equations to a system of equations describing the one-dimensional kinetic Ising model, which allows us to solve the governing equations exactly. In Sec. III, we investigate the diffusion-controlled catalysis process with deposition in a mean-field approximation. We develop a scaling theory to describe the long-time behavior of the process and find that the density of the total number of islands grows as $t^{1/5}$ in the long-time limit. We then examine the reaction-controlled catalysis process. For a homogeneous case where the monomer-island reaction rates vary as k^γ with the island size k, we find that the island-size distribution function exhibits scaling but the exponents are different for $\gamma<\frac{1}{2}$ and $\gamma>\frac{1}{2}$. In Sec. IV, we discuss peculiarities of the diffusion-controlled model, which take place on low-dimensional substrates. For $d=2$, we derive logarithmic corrections to the mean-field results while for $d=1$ we develop a modified rate-equation approach which, in particular, predicts that the number of islands grows as $t^{1/7}$ as $t\rightarrow\infty$. Finally, we summarize our results in Sec. V.

II. REACTION PROCESS WITHOUT DEPOSITION

Let us first consider the *diffusion-controlled* reaction process without deposition in the mean-field limit. There are two types of islands in the system: A islands and B islands. Denote by $A_k(t)$ and $B_k(t)$ the concentrations of A and B islands of size k, or k-mers, at time t. If we ignore fluctuations in the densities and shapes of the islands, the kinetics can be described by rate equations

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$$\frac{dA_1}{dt}=K_2A_2B_1 - A_1\left[K_1A_1+\sum_{j=1}^{\infty}K_jA_j+K_1B_1+\sum_{j=1}^{\infty}K_jB_j\right] , \tag{1a}$$

$$\frac{dA_j}{dt}=A_1(K_{j-1}A_{j-1}-K_jA_j) +B_1(K_{j+1}A_{j+1}-K_jA_j) , \quad j\geq 2 , \tag{1b}$$

governing the evolution of A_k and symmetrical equations for B_k. The rates of aggregation $A_1+A_j \rightarrow A_{j+1}$ and $B_1+B_j \rightarrow B_{j+1}$, and evaporation $B_1+A_j \rightarrow A_{j-1}$ and $A_1+B_j \rightarrow B_{j-1}$ are implicitly assumed equal and denoted by K_j. This is a reasonable assumption for diffusion-controlled processes if the diffusivities of both A and B monomers are *equal.*

Note that rate equations for similar aggregation-annihilation processes but in the opposite extreme of equal diffusivities of monomers and islands have been investigated in [14]. Another related system of equations describing the single-species aggregation process with diffusing monomers and immobile islands follows from Eqs. (1) by letting $B_j \equiv 0$. That system of equations with homogeneous reaction rates $K_j = j^{\gamma}$ has been studied previously [15,16]. For models with $0 \leq \gamma \leq 1$, it was found that the island-size distribution approach to final states was strongly dependent on the initial conditions [16].

Consider the most interesting symmetrical case, $A_k = B_k$, and denote by C_k the concentration of k-mers of any type. Introducing the auxiliary time variable T,

$$T=\int_0^t dt' C_1(t') , \tag{2}$$

we arrive at the *linear* equations for $C_k(T)$:

$$\frac{dC_1}{dT}=K_2C_2-2K_1C_1-2\sum_{j=1}^{\infty}K_jC_j , \tag{3a}$$

$$\frac{dC_j}{dT}=K_{j-1}C_{j-1}-2K_jC_j+K_{j+1}C_{j+1} , \quad j\geq 2 . \tag{3b}$$

Upon summing of Eqs. (3), one can find the kinetic equation for the density of the total number of islands $N(T)$, $N(T)=\sum_{j\geq 1}C_j(T)$:

$$\frac{dN}{dT}=-K_1C_1-2\sum_{j=1}^{\infty}K_jC_j . \tag{4}$$

Similarly, the next two moments of the island-size distribution function $C_j(T)$, $\theta(T)=\sum_{j\geq 1}jC_j(T)$ and $M(T)=\sum_{j\geq 1}j^2C_j(T)$, satisfy the equations

$$\frac{d\theta}{dT}=-2\sum_{j=1}^{\infty}K_jC_j , \quad \frac{dM}{dT}=0 . \tag{5}$$

The second equation indicates that $M=\text{const}$. For the present aggregation-evaporation process, a k-mer would typically arise from the merging of k^2 monomers of *both* species. Therefore, we conclude that the conservation of the second moment in the aggregation-evaporation process could be considered as the conservation of mass in the "underlying" merging process. In contrast, for the usual aggregation process the first moment, i.e., the mass of the system, is always conserved.

For further analysis we should specify the reaction rates. Consider the model of structureless islands in which both mobile monomers and immobile islands occupy single lattice points. On the level of rate equations, structureless islands correspond to the constant reaction rates, $K_j=\text{const}$. One can set the constant equal to one without loss of generality. This leads to the kinetic equations

$$\frac{dC_1}{dT}=C_2-2C_1-2N , \quad \frac{dN}{dT}=-C_1-2N , \tag{6}$$

$$\frac{dC_j}{dT}=C_{j-1}-2C_j+C_{j+1} , \quad j\geq 2 . \tag{7}$$

Introducing now the auxiliary variables $C_{-j}\equiv C_j$ and $C_0 \equiv -2N$, one can rewrite Eqs. (6) in the form of (7) with $j=1$ and 0, respectively. Moreover, the variables C_j satisfy (7) for all integer j. Note that Eqs. (7) arise in a number of models for one-dimensional systems with nearest-neighbor coupling including, e.g., the kinetic Ising model with zero-temperature Glauber dynamics [17], the chain of harmonically coupled Brownian particles [18], and the monomer-monomer catalysis without diffusional relaxation [10]. A general solution to Eqs. (7) for the infinite chain subject to arbitrary initial conditions $C_j(0)$ is

$$C_j(T)=e^{-2T}\sum_{m=-\infty}^{\infty}C_m(0)I_{j-m}(2T) . \tag{8}$$

Here I_m denotes the modified Bessel function of the order m. Additionally, the definition of C_j for $j\leq 0$ implies $C_{-j}(0)=C_j(0)$ and $C_0(0)=-2\sum_{j\geq 1}C_j(0)$. Specifying the exact solution for the monodisperse initial conditions, $C_j(t=0)=\delta_{j1}$ for $j\geq 1$, gives

$$C_j(T)=e^{-2T}[I_{j-1}(2T)-2I_j(2T)+I_{j+1}(2T)] , \quad j\geq 1 . \tag{9}$$

In particular, the density of monomers $C_1(T)=e^{-2T}[I_0(2T)-2I_1(2T)+I_2(2T)]$ vanishes at $T=T_f\cong 0.772\,563$, which corresponds to the value $t=\infty$ of the physical time t. All other concentrations are finite at $t=\infty$. Note also that in terms of the physical time t, the density of monomers decays exponentially.

$$C_1(t)\sim e^{-\mu t} , \tag{10}$$

with

$$\mu=2N(\infty)-C_2(\infty)=e^{-2T_f}[I_1(2T_f)-I_3(2T_f)] \cong 0.200\,104 .$$

Furthermore, all other densities also approach their final values exponentially, $C_j(\infty)-C_j(t)\sim e^{-\mu t}$.

The distribution $C_j(t)$ does not reach a scaling form and instead falls to the frozen state depending on initial conditions. This is reminiscent of the behavior of pure aggregation models with diffusion monomers and immobile islands [15,16]. A qualitative explanation of this unusual behavior is provided by using the notion of internal time T, see [16]. Since this internal time is actually the relevant time variable and since it changes in a finite time interval, the scaling behavior just has no "time" to develop. Nevertheless, the "deviation" from the frozen state still has a self-similar form. Indeed, making use of the asymptotic relation $I_j(2T) \to T^j/j!$ for $j \gg 1$ one can find that the ratio

$$C_j(t)/C_j(\infty) \to \exp[-j(1-T/T_f)] \tag{11}$$

scales in the limit $j \to \infty$ and $T \to T_f$ with $j(T_f - T) \sim jC_1(t) \sim je^{-\mu t}$ kept finite.

Our previous treatment has assumed that islands are structureless and the dimensionality of the substrate is large enough so that the mean-field approximation provides an adequate description of the kinetics. Let us consider these assumptions more carefully. One can try to take into account the structure of islands by using the general rate equations (3). For the diffusion-controlled catalytic processes, the rate K_j of the reactions $C_1 + C_j \to C_{j\pm 1}$ can be estimated by applying Smoluchowski's formula [19] $K_j \sim D(R_1 + R_j)^{d-2}$ in d dimensions (for $d > 2$). Here D is the atomic diffusion coefficient, and R_1 and R_j are the radii of atoms and islands containing j atoms. This result is based on considering the j island as an ideal spherical stationary trap of radius $R_1 + R_j$, which is surrounded by a cloud of diffusing point particles that are captured upon contact with the trap. The reaction rate is identified as the flux of particles to the trap. If the islands are compact, Smoluchowski's formula gives $K_j \sim j^{1-2/d}$ for $j \gg 1$. For fractal islands having the fractal dimension D_f, one has $R_j \sim j^{1/D_f}$ and therefore $K_j \sim j^{(d-2)/D_f}$. Thus, in the most interesting case $d = 2$, and only for $d = 2$, the structure of islands becomes unimportant and hence the model of structureless islands may be applied.

In fact, for $d = 2$ the situation is more delicate because this case demarcates different behaviors of reaction rates for $d > 2$ and $d < 2$. Indeed, if $d > 2$ the density of Brownian particles absorbed by a trap reaches a stationary profile. On the other hand, for $d \le 2$ the flux onto a trap does not reach a stationary value. However, in two dimensions the flux tends to $4\pi D/\ln(Dt/R^2)$ (see, e.g., [20]) and hence only logarithmic corrections to the mean-field results for structureless islands are expected.

Another limitation of the previous treatment is an assumption that the catalytic process is diffusion controlled. In the opposite limiting case of the reaction-controlled catalytic process, the mixing is perfect and one can apply the mean-field description for a substrate of arbitrary dimensionality. However, for realistic models in which the islands have finite size, the reaction rates depend on the size. It is difficult to establish such dependence without going into the details of island forms. The only general feature is the fact that K_j/j is bounded. It is valid for islands of arbitrary shape since the number of active sites on an island cannot increase faster than the island size. It turns out that the extreme case $K_j = j$ is solvable. The system evolves onto a stationary state, which is strongly dependent on the initial state. The behavior very similar to the case of structureless islands is found. Since the derivation of the exact solution is rather lengthy, it is not included here.

III. REACTION PROCESS WITH DEPOSITION

In the model with deposition of monomers, we still restrict ourselves to the regime of low coverage where possible coalescence of islands may be ignored. We shall focus again on the most interesting case of equal deposition rates of both species. For the case of structureless islands, we get

$$\frac{dC_1}{dt} = I + DC_1(C_2 - 2C_1 - 2N) , \tag{12}$$

$$\frac{dC_j}{dt} = DC_1(C_{j-1} - 2C_j + C_{j+1}) , \quad j \ge 2 , \tag{13}$$

where I is the rate of deposition. We will measure the lengths in the units of the lattice constant. So the densities become dimensionless while the rates of diffusion D and deposition I have the same dimension of $(\text{time})^{-1}$. The ratio $\lambda = D/I$ is an important dimensionless parameter that is usually very large.

I could not find an analytical solution to this infinite system of nonlinear differential equations. However, it is possible to analyze the long-time behavior by assuming that the solution approaches a scaling form as $t \to \infty$. Then one can check the self-consistency of the results. Heuristically, the existence of scaling can be explained by the slow decay of the density of monomers. Therefore, the internal time T varies in an infinite time interval thus providing "enough" time for the scaling to be developed.

Let us assume that asymptotically the concentration distribution function $C_j(T) = C(j,T)$ may be considered as a smooth function of j at least for $j \gg 1$. Let us define the internal time by $T = D\int_0^t dt' C_1(t')$, which differs from (2) by factor D to make the internal time dimensionless. Replacing now the difference operator on the right-hand side of Eq. (13) by its differential approximation shows that $C(j,T)$ satisfies the diffusion equation

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial j^2} . \tag{14}$$

Equations (14) and (12) suggest the scaling ansatz of the form

$$C(j,T) \simeq \lambda^{-a} T^{-b} F(\eta) , \quad \eta = \frac{j}{\sqrt{2T}} . \tag{15}$$

To find the exponents a and b let us compute the asymptotic behavior of the density of the total number of islands N, $N = \sum_{j \ge 1} C_j$, by two complementary methods. First, replacing the sum by the integral yields

$$N \to \int_0^\infty dj\, C(j,T) \simeq \lambda^{-a} \frac{\sqrt{2T}}{T^b} \int_0^\infty d\eta\, F(\eta) . \tag{16}$$

Second, the kinetic equation $dN/dt = I - DC_1(C_1 + 2N)$ shows

$$N \to \frac{1}{2\lambda C_1} \simeq \lambda^{a-1}\frac{T^b}{2F(0)} \ . \tag{17}$$

By comparing (16) and (17), we determine the exponents $a=\frac{1}{2}$, $b=\frac{1}{4}$, and an additional normalization relation

$$2\sqrt{2}F(0)\int_0^\infty d\eta\, F(\eta)=1 \ . \tag{18}$$

To derive the complete scaling solution, let us substitute the scaling form of (15) with $b=\frac{1}{4}$ into Eq. (14). This gives

$$\frac{d^2F}{d\eta^2}+\eta\frac{dF}{d\eta}+\tfrac{1}{2}F=0 \ . \tag{19}$$

The substitution $F(\eta)=e^{-\eta^2/4}G(\eta)$ transforms (19) to

$$\frac{d^2G}{d\eta^2}-\frac{\eta^2}{4}G=0 \ . \tag{20}$$

The general solution to this equation can be written in terms of the parabolic cylinder function of the order $-\frac{1}{2}$, $G(\eta)=AD_{-1/2}(\eta)+BD_{-1/2}(i\eta)$. The asymptotic behavior at $\eta\to\infty$ implies $B=0$, while the normalization condition (18) gives $A=\frac{1}{2}$. The latter result has been derived after straightforward calculations making use of the identity $\int_0^\infty d\eta\, F(\eta)=-2F'(0)$, which directly follows from Eq. (19), the values of $D_{-1/2}(0)$ and $D'_{-1/2}(0)$ (see, e.g., [21])

$$D_{-1/2}(0)=\frac{\pi^{1/2}2^{-1/4}}{\Gamma(\frac{3}{4})} \ , \quad D'_{-1/2}(0)=-\frac{\pi^{1/2}2^{1/4}}{\Gamma(\frac{1}{4})} \ , \tag{21}$$

and the identity $\Gamma(\frac{1}{4})\Gamma(\frac{3}{4})=\pi/\sin(\pi/4)=\pi\sqrt{2}$.

Thus, we have found the scaling solution,

$$C(j,T)\simeq\tfrac{1}{2}\lambda^{-1/2}T^{-1/4}\exp\left[-\frac{j^2}{8T}\right]D_{-1/2}\left[\frac{j}{\sqrt{2T}}\right] , \tag{22}$$

for the island-size distribution function. It is straightforward to check that $C(j,T)$ is indeed a smooth function of j as well as the fact that in the long-time limit the discrete second derivative $C_{j-1}-2C_j+C_{j+1}$ may be replaced by the continuous second derivative.

Several asymptotics of the island-size densities $C_j(T)$ can be readily found, e.g.,

$$C_j(T)\simeq\frac{\sqrt{\pi}}{2^{5/4}\Gamma(\frac{3}{4})}\lambda^{-1/2}T^{-1/4} \quad \text{for } j\ll\sqrt{T} \tag{23}$$

and

$$C_j(T)\simeq 2^{-3/4}\lambda^{-1/2}j^{-1/2}\exp\left[-\frac{j^2}{4T}\right] \quad \text{for } j\gg\sqrt{T} \ . \tag{24}$$

Combining the definition of the internal time and the asymptotic expression for the density of monomers gives the relation between physical and internal times

$$T\simeq A\lambda^{2/5}(It)^{4/5} \ , \tag{25}$$

with a numerical factor $A=2^{-13/5}5^{4/5}\pi^{2/5}[\Gamma(\frac{3}{4})]^{-4/5}\cong 0.803\,028$.

Neglecting numerical factors we obtain the following asymptotic behaviors for the density of monomers, islands, and the average number of atoms per island, $S(t)$:

$$\begin{aligned} &C_1(t)\sim\lambda^{-3/5}(It)^{-1/5} \ ,\\ &N(t)\sim\lambda^{-2/5}(It)^{1/5} \ ,\\ &S(t)\sim\lambda^{1/5}(It)^{2/5} \ . \end{aligned} \tag{26}$$

Note that in the model of single-species growth with diffusing monomers and immobile islands, the island-size distribution also scales so that $C_1\sim\lambda^{-2/3}t^{-1/3}$ and $N\sim\lambda^{-1/3}t^{1/3}$; see, e.g., [16,22–28]. Thus, we reach an intuitively appealing conclusion that in the present model of two-species growth both $N(t)$ and $S(t)$ increase more slowly.

Since we have ignored the coalescence of islands, we should check that the coverage is small. The coverage θ is given by the second moment of the island-size distribution, $\theta(t)=\sum_{j\geq 1}jC_j(t)\sim\lambda^{-1/5}(It)^{3/5}$. Hence the low-coverage condition $\theta\ll 1$ implies an upper bound on the time $It\ll\lambda^{1/3}$. Combining this with Eq. (26) gives upper bounds on the density of islands $N\ll N_{\max}=\lambda^{-1/3}$ and for the average number of atoms per islands $S\ll S_{\max}=\lambda^{1/3}$.

It is useful to reexpress the asymptotic relations (26) as the functions of coverage θ:

$$\begin{aligned} &C_1(\theta)\sim\lambda^{2/3}\theta^{-1/3} \ ,\\ &N(\theta)\sim\lambda^{-1/3}\theta^{1/3} \ ,\\ &S(\theta)\sim\lambda^{1/3}\theta^{2/3} \ . \end{aligned} \tag{27}$$

A surprising feature of these asymptotics is that they *coincide* with the asymptotics describing the single-species growth model in which the coverage and the time are proportional to each other. However, the details of the island-size distribution are very different in both models. In the two-species model, the island-size distribution is flat for sufficiently small islands, $j\ll S$, while in the single-species model it has a sharp peak at $j\sim S$.

Previous results have been established for the case of structureless islands in the diffusion-controlled limit. As has been argued earlier, even for general diffusion-controlled catalytic processes in the low-coverage limit, the point-island rate equations are expected to provide an accurate description except for logarithmic corrections. In the opposite limiting case of reaction-controlled catalytic processes, the reaction rate K_j depends on the island size j. It is natural to assume that K_j scales as the island perimeter. Thus, in this limit for the case of compact islands on a two-dimensional substrate $K_j\sim j^\gamma$ with $\gamma=\frac{1}{2}$, while for fractal islands we expect $\gamma=1/D_f$ and hence $\frac{1}{2}<\gamma<1$. Since the proportionality factors do not influence the scaling behavior, we will ignore them and consider a general homogeneous form $K_j=j^\gamma$. In the long-time limit, the island-size distribution function satisfies the modified diffusion equation

$$\frac{\partial C_j}{\partial T}=\frac{\partial^2(j^\gamma C_j)}{\partial j^2} \ , \tag{28}$$

while the rate equation for monomer density implies

$$2\lambda C_1 \sum_{j=1}^{\infty} j^{\gamma} C_j = 1 \; . \tag{29}$$

The scaling ansatz compatible with (28) and (29) has the form

$$C_j(T) \simeq \lambda^{-1/2} j^{-\gamma} T^{-1/(4-2\gamma)} F(\eta) \; , \quad \eta = jT^{-1/(2-\gamma)} \; . \tag{30}$$

Relating then the physical and internal times, we can reexpress the basic quantities in terms of λ and t:

$$C_1 \sim \lambda^{-\alpha}(It)^{-\beta} \; , \quad N \sim \lambda^{-p}(It)^{q} \; , \quad S \sim \lambda^{r}(It)^{z} \; , \tag{31}$$

with the exponents

$$\alpha = \frac{3-\gamma}{5-2\gamma} \; , \quad q = \frac{1-2\gamma}{5-2\gamma} \; , \qquad \beta = r = \frac{1}{5-2\gamma} \; , \quad p = z = \frac{2}{5-2\gamma} \; . \tag{32}$$

Since the total number of islands is an increasing function of time, at least in the low-coverage limit, the exponent q must be non-negative. Thus, Eq. (32) is expected to hold if $\gamma \le \frac{1}{2}$. (In fact, in the special case $\gamma = \frac{1}{2}$ logarithmic corrections should appear. A separate analysis is required, see [16,22,28] for a similar treatment in the model of single-species growth.)

For the case $\gamma > \frac{1}{2}$, we assume that the total number of islands reaches the constant, $N \to \lambda^{-p}$. Ignoring for the moment the λ dependence, we make use of the scaling form $C_j \sim t^{-\bar{\beta}} j^{-\gamma} F(jt^{-z})$ to find $N \sim t^{-\bar{\beta}+z(1-\gamma)}$ and $M = \sum j^2 C_j \sim t^{-\bar{\beta}+z(3-\gamma)}$. Since N is constant and $M = It$, we obtain $\bar{\beta} = z(1-\gamma)$ and $1+\bar{\beta} = z(3-\gamma)$. Solving for $\bar{\beta}$ and z gives $\bar{\beta} = (1-\gamma)/2$, $z = \frac{1}{2}$. Proceeding in a similar way we find all the exponents:

$$\alpha = \frac{2+\gamma}{4} \; , \quad \beta = \frac{\gamma}{2} \; , \quad p = \tfrac{1}{2} \; , \quad q = 0 \; , \qquad r = \tfrac{1}{4} \; , \quad z = \tfrac{1}{2} \quad (\gamma > \tfrac{1}{2}) \; . \tag{33}$$

Notice that an implicit assumption on the behavior of the scaling function in the small size limit, $F(\eta) \to F(0) > 0$ as $\eta \to 0$, turns out to be correct only in the case $\gamma < \frac{1}{2}$. In the present case $\gamma > \frac{1}{2}$ we instead assumed $F(\eta) \sim \eta^{\omega}$ and found $\omega = 2\gamma = 1$. This explains the difference between the exponent β describing the monomer decay and the exponent $\bar{\beta}$ describing the decay of the island-size distribution.

IV. REACTION PROCESS ON LOW-DIMENSIONAL SUBSTRATES

Returning to the diffusion-controlled process and noting that $d=2$ is the critical dimension for diffusion-limited island growth, we conclude that the rate-equation approximation cannot be applied for low dimensions, i.e., when the substrate has dimension $d=1$ or $d=2$. In fact, the most important two-dimensional case is marginal; therefore, the correct behavior is provided by the mean-field approximation up to logarithmic corrections. To figure out these corrections, we adapt an approach from the single-species study [24] to the present situation. Starting from the one-dimensional case, let us first try to obtain an approximate differential equation for the density of monomers. If τ is a collision time, one has

$$\frac{dC_1}{dt} = I - \frac{C_1}{\tau} \; . \tag{34}$$

In the long-time limit, the density of monomers is very small and we can ignore monomer-monomer reactions. Islands are distributed on a lattice with the density N, $C_1 \ll N \ll 1$, and they play a role of traps. When a monomer hops on such a lattice with rate D, it will be trapped after a typical time [29]

$$\tau \sim \begin{cases} (DN)^{-1} \; , & \text{if } d > 2 \\ (DN)^{-1} \ln \left[\dfrac{1}{N} \right] \; , & \text{if } d = 2 \\ (DN^2)^{-1} \; , & \text{if } d = 1 \; . \end{cases} \tag{35}$$

By combining (35) and (34) for $d > 2$, we obtain a governing equation for the monomer density, which agrees with Eq. (12) in the long-time limit. In contrast, for $d=1$ and 2 we obtain nonquadratic reaction term: DC_1N^2 in the former case and $DC_1N/\ln(1/N)$ in the latter. Similar corrections to the mean-field rate equations appeared in equations for all other densities. So let us write down the modified rate equations that differ from the mean-field ones just at this point and examine the long-time behavior. We expect that such an approach provides asymptotically correct results as it indeed took place in a number of similar situations (see, e.g., [30] and references therein). One cannot expect that numerical coefficients in reactions terms are correct; therefore, we prescribe to these coefficients the same values as in the mean-field equations.

In one dimension we have

$$\frac{dC_1}{dt} = I + DC_1N(C_2 - 2C_1 - 2N) \; , \tag{36}$$

$$\frac{dC_j}{dt} = DC_1N(C_{j-1} - 2C_j + C_{j+1}) \; , \quad j \ge 2 \; . \tag{37}$$

Introducing the internal time T,

$$T = \int_0^t dt' DC_1(t')N(t') \; , \tag{38}$$

and going to the continuum approximation, we can rewrite Eq. (37) in the previous form of the diffusion equation (14). Taking the scaling ansatz of the form

$$C(j,T) \simeq \lambda^{-a} T^{-b} F_1(\eta) \; , \quad \eta = \frac{j}{\sqrt{2T}} \; , \tag{39}$$

we again compute N by two independent methods to find

$$N(T) = \sum_{j=1}^{\infty} C_j(T) \simeq \lambda^{-a} \frac{\sqrt{2T}}{T^b} \int_0^{\infty} d\eta \, F_1(\eta) \tag{40}$$

and

$$N(T) \simeq (2\lambda C_1)^{-1/2} \simeq \lambda^{(a-1)/2} \frac{T^{b/2}}{\sqrt{2F_1(0)}} \; . \tag{41}$$

These two expressions allow us to determine the exponents $a=\frac{1}{3}$, $b=\frac{1}{3}$, and to obtain a normalization condition

$$2\sqrt{F_1(0)}\int_0^\infty d\eta\, F_1(\eta)=1 \; . \tag{42}$$

By inserting the scaling ansatz (30) with $b=\frac{1}{3}$ into Eq. (14), we arrive at

$$\frac{d^2F_1}{d\eta^2}+\eta\frac{dF_1}{d\eta}+\tfrac{2}{3}F_1=0 \; . \tag{43}$$

A solution to Eq. (43) can be written in terms of the parabolic cylinder function $D_{-1/3}(\eta)$, $F_1(\eta)=A\exp(-\eta^2/4)D_{-1/3}(\eta)$. Therefore,

$$C(j,T)\simeq A\lambda^{-1/3}T^{-1/3}\exp\left[-\frac{j^2}{8T}\right]D_{-1/3}\left[\frac{j}{\sqrt{2T}}\right] . \tag{44}$$

Here the constant A can be determined from the normalization condition (42). A lengthy calculation gives $A=[\Gamma(\frac{2}{3})]^{1/3}[\Gamma(\frac{1}{6})]^{2/3}\pi^{-1/2}2^{-5/6}3^{-2/3}\cong 0.528\,952$.

Combining the relation between T and t [given by Eqs. (38)] and the asymptotics $C_1(T)\sim\lambda^{-1/3}T^{-1/3}$, $N(T)\sim\lambda^{-1/3}T^{1/6}$ gives the relation between the (dimensionless) original time It and the internal time T, $It\sim\lambda^{-1/3}T^{7/6}$. Then we find the coverage $\theta\sim\lambda^{-1/3}T^{2/3}\sim\lambda^{-1/7}(It)^{4/7}$. So in one dimension we get

$$\begin{aligned} &C_1\sim\lambda^{-3/7}(It)^{-2/7}\sim\lambda^{-1/2}\theta^{-1/2} \; , \\ &N\sim\lambda^{-2/7}(It)^{1/7}\sim\lambda^{-1/4}\theta^{1/4} \; , \\ &S\sim\lambda^{1/7}(It)^{3/7}\sim\lambda^{1/4}\theta^{3/4} \; . \end{aligned} \tag{45}$$

Note that for the single-species growth model, the corresponding asymptotic results read $C_1\sim\lambda^{-1/2}t^{-1/2}$. Thus the θ dependence is again the same for both single-species and two-species models, although the details of island-size distributions are different. Note also that the low-coverage condition indicates that the present theory can be applied when $N\ll N_{\max}=\lambda^{-1/4}$.

On the two-dimensional substrate, the governing equations are

$$\frac{dC_1}{dt}=I+DC_1\frac{1}{\ln(1/N)}N(C_2-2C_1-2N) \; , \tag{46}$$

$$\frac{dC_j}{dt}=DC_1\frac{1}{\ln(1/N)}(C_{j-1}-2C_j+C_{j+1}) \; , \quad j\geq 2 \; , \tag{47}$$

Introducing the internal time T,

$$T=\int_0^t dt'\frac{DC_1(t')}{\ln[1/N(t')]} \; , \tag{48}$$

we again obtain the diffusion equation for $C_j(T)$. We will assume the scaling ansatz of the form

$$C(j,T)\simeq\lambda^{-1/2}T^{-1/4}L^{\nu}F_2(\eta) \; , \quad \eta=\frac{j}{\sqrt{2T}} \; , \tag{49}$$

which differs from the mean-field one by some power of a logarithmic factor L, to be specified below. Repeating the steps employed in analogous previous computations, we get $\nu=\frac{1}{2}$ and $L=\ln(\lambda^2/It)$ as well as the normalization condition, which is identical to the mean-field one. It is then straightforward to verify that the scaling function F_2 is identical to the mean-field scaling function, $F_2(\eta)=\exp(-\eta^2/4)D_{-1/2}(\eta)$.

Thus, on the two-dimensional substrate

$$\begin{aligned} &C_1\sim(\lambda/L)^{-3/5}(It)^{-1/5}\sim(\lambda/L)^{-2/3}\theta^{-1/3} \; , \\ &N\sim(\lambda/L)^{-2/5}(It)^{1/5}\sim(\lambda/L)^{-1/3}\theta^{1/3} \; , \\ &S\sim(\lambda/L)^{1/5}(It)^{2/5}\sim(\lambda/L)^{1/3}\theta^{2/3} \; . \end{aligned} \tag{50}$$

By comparison with the mean-field results we conclude that the main difference is the "renormalization" of the deposition rate: $\lambda\to\lambda/L$. Note also that the low-coverage condition yields $N\ll N_{\max}=[\ln(\lambda)/\lambda]^{1/3}$.

V. SUMMARY

A model that describes the kinetics of the monomer-monomer catalytic reaction with diffusional relaxation is proposed. The model incorporates adsorption, diffusion of single atoms, aggregation of similar-species atoms into immobile islands, and desorption of adjacent dissimilar-species atoms. The present model is based on a few fundamental kinetic mechanisms that may equally arise in very different situations; hence, the model may describe different physical processes.

This study has focused on the case of structureless islands in the low-coverage limit. We have found a surprising equivalence of the rate equations describing evolution of our model without deposition and equations governing the kinetics of the one-dimensional Ising model with Glauber dynamics at zero temperature. This has allowed us to obtain a closed-form analytical solution and to find out that the system approaches a frozen state strongly dependent on the initial conditions. For the system with deposition, we have found that the island-size distribution exhibits the scaling behavior. These results have been derived on the level of rate equations, which provide an appropriate description for substrate of dimensionality $d>2$. A generalization for one- and two-dimensional substrates based on a modified rate-equation approach also reveals the scaling behavior. While our results are only appropriate for the low-coverage limit, we have argued that other idealizations of the present surface reaction model such as the structureless condition are less significant, at least for the most important case of the two-dimensional substrate [23,25–27].

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