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# Structure of a Langmuir-Hinshelwood reaction interface

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We have performed Monte Carlo simulations to investigate the structure of the interface between the two reactants in a Langmuir-Hinshelwood reaction. A square lattice-gas model is employed in the simulations. The time evolution of an initially flat interface between two domains of the reactants is studied. It is found that the particle density, averaged in a direction parallel to the initial, flat interface, obeys a diffusion equation. We provide an argument to show that the effective diffusion coefficient in this reaction model is the same as that in a diffusion model in which one of the reactants is considered to be a diffusing particle and the other reactant is considered to be a vacant site on the lattice. This implies that the average concentration profile of the reactants can be described by a diffusion equation even though the system consists of particles which are reacting but not diffusing. The appropriate diffusion coefficient is equal to the square of the lattice constant multiplied by the reaction rate for a reactive nearest-neighbor pair. The fractal dimension of the external perimeter of the reactant domains is found to be 1.33 ± 0.01, which suggests that it is equal to the fractal dimension of $\frac{4}{3}$ of the external perimeter in diffusion. It is found that the fractal dimension of the external perimeter depends upon whether the adsorption rate is infinitely higher than the reaction rate or vice versa. The roughness of the external perimeter in our reaction model scales with time as $t^{\beta}$, where $\beta \approx 0.45 \pm 0.01$. This roughening is faster than in the case of diffusion where $\beta = \frac{2}{7}$ and is a consequence of the correlation in site occupancy between particles of the same species. The roughening exponent here is also larger than that in the Ising model where $\beta = \frac{1}{4}$, and we argue that this is responsible for the slow poisoning (i.e., loss of reactivity) of this reactive lattice gas.

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## I. INTRODUCTION

The study of interfaces has been one of the most active areas in statistical physics in recent years [1–6]. In particular, the structure of a nonequilibrium interface and the dynamics of its roughening are interesting issues. An interface between two phases, one of which is growing into the other, can be described by the Kardar-Parisi-Zhang (KPZ) equation, which is a stochastic equation obtained by appealing only to symmetry and conservation laws [4,5]. The KPZ equation includes an effective surface tension, the dependence of the interface velocity upon the slope of the interface, and noise which is $\delta$-function correlated in time and space. It has been used successfully to understand various deposition models [7]. In these models, the noise is the result of the stochastic nature of adsorption and desorption, and it describes the random addition or removal of single particles at the interface. There are, however, interfacial phenomena in which the noise results from the addition or removal of clusters of particles at the interface. An example which has been investigated in an interesting paper by Sapoval, Rosso, and Gouyet is the evolution of the diffusion hull [8]. It was shown that the hull in the case of diffusion has the same fractal dimension as the percolation hull. The noise that occurs in the evolution of the hull results from clusters joining or breaking away from the hull and has been called intercalation noise [9]. Since these events involve the addition or removal of clusters with a variable number of particles, the nature of the noise is different from that appropriate for the deposition models in which single particles are involved.

Another type of interface in which intercalation noise is expected to play an important role is the interface in a Langmuir-Hinshelwood reaction. In a previous study we have investigated the time evolution of a model of a surface reaction on a square lattice in which particles of two species react (and the product immediately desorbs) if they are nearest neighbors to each other [10]. There we treated the case in which the reaction rate is infinitely higher than the adsorption rate. Thus, at the interface of two domains of the reactants, a zone of vacant sites forms and this is where the surface reaction occurs. By including an attractive interaction between particles of the same species, the reaction rate of a nearest-neighbor pair can be made dependent upon the neighborhood of the pair. It was shown that with such an attractive interaction the interface roughens with time as $t^{1/4}$, and it is possible to understand this phenomenon using the KPZ equation [10]. When this attractive interaction is not present, the interface roughens faster, scaling with time as $t^{\beta}$ with $\beta \approx 0.5$. In this case, intercalation noise is important in the interfacial roughening.

In order to pursue the connection between the interface in the Langmuir-Hinshelwood reaction and the interface in diffusion, we have performed Monte-Carlo simulations of a slightly different Langmuir-Hinshelwood reaction model. In the previous model that we investigated, the reaction rate is infinitely higher than the adsorption rate. Hence vacant sites are present on the lattice. In the model studied in this paper, the adsorption rate is chosen to be infinitely higher than the reaction rate, i.e., each time a nearest-neighbor pair of particles reacts and leaves the lattice, the vacated sites are filled immediately by adsorbing particles. Here it is appropriate to mention work that has been done on a related Langmuir-Hinshelwood model [11–13]. Each half of a lattice can be populated by a lattice gas of low density of each species. The lattice-gas particles are then allowed to diffuse, and reaction occurs upon the "collision" of two particles of different species. The width of the reaction zone has been found to scale with time as $t^{1/6}$ [11–13]. In this model the interface where the two domains of lattice gases meet is difficult to define since the fractional coverage in the domains occupied by each of the lattice-gas species is not high. In our investigations, each domain is occupied with a fractional coverage of unity. Hence the interface can be defined rather unambiguously.

## II. MODEL

The model that we investigate here is described by the following chemical equations:

$$A(\mathrm{g}) + v \rightarrow A(\mathrm{s}),$$

$$B(\mathrm{g}) + v \rightarrow B(\mathrm{s}),$$

$$A(\mathrm{s}) + B(\mathrm{s}) \rightarrow AB(\mathrm{g}) + 2v.$$

The first two steps are adsorption events and the third step is the reaction between two adsorbed reactant particles. Vacancies on the lattice are denoted by $v$, the gas phase by (g), and adsorbed particles by (s). The simulations begin with a square lattice one half of which is initially populated with $A$ and the other half of which is initially populated with $B$. The interface between the $A$ and the $B$ domains is initially flat and chosen to be along one of the principal axes. In the long time limit, we do not believe that the results depend upon this particular choice of initial conditions. The horizontal axis is chosen to be the $x$ axis and the vertical axis the $z$ axis. The initially flat interface is parallel to the $x$ axis.

The simulations are performed as follows. A nearest-neighbor pair is picked at random. For each such attempt, time is incremented by one Monte Carlo step. This is repeated until an $AB$ pair is picked. Then reaction occurs and both the picked $A$ and $B$ particles are removed from the lattice. The two vacancies thus formed are filled immediately. Each vacancy is filled with $A$ or $B$, with an equal probability of 0.5 for each reactant. The procedure is then repeated. Using this simulation procedure implies that we take the adsorption rate to be infinitely higher than the reaction rate. Any vacant site on the lattice is filled immediately, i.e., the total fractional coverage of adsorption on the lattice is always unity.

We also performed simulations with the above procedure except that each chosen $AB$ pair is not removed from the lattice but rather flipped with a probability of 0.5, i.e., $AB$ changes to $BA$ or remains as $AB$ with equal probability. This simulates diffusive particle hopping if we consider $A$ to be particles and $B$ to be vacancies. The simulations of this diffusion model are performed in order to provide a comparison with the reaction model.

## III. RESULTS AND DISCUSSION

When the reaction proceeds, the originally flat interface between the two domains becomes rough. Clusters of one species will be formed in the domain of the other species. Thus, the reactive zone, which was originally limited to the two neighboring rows at the interface, now becomes wider. Note that there are two kinds of boundaries between $A$ and $B$ particles. The first kind is the interface between the two domains of $A$ and $B$, and the second kind are the interfaces formed by clusters of $B$ particles in domain $A$ or clusters of $A$ particles in domain $B$.

One quantity which is of interest is the width of the region where the concentrations of both A and B are nonzero. For the reaction-diffusion model studied in Refs. [11–13], this width was shown to scale as $t^{1/2}$. We can measure this width simply as follows. Assign spin +1 to particles of species $A$ and spin −1 to particles of species $B$. Then, following Swendsen [14], the gradient of the magnetization perpendicular to the interface can be defined as

$$g(z) = \nabla M(z)/[M(\infty) - M(-\infty)], \tag{3.1}$$

where $M(z)$ is the magnetization at height $z$ averaged over all $x$. The width $w_r$ is then defined as the root-mean-square interface position given by the distribution $g(z)$. The simulation results for $w_r$ for both the reaction model and the diffusion model are plotted in Fig. 1.

It is clearly seen that the interface width measured by $w_r$ is the same in the two models. This implies the interesting result that the average magnetization $M(z)$ in the reaction model obeys the diffusion equation even though the interface evolution is driven by a Langmuir-Hinshelwood reaction and the reactants are not mobile. As will be shown below, the diffusion coefficient describing $M(z)$ in the reaction model is the same as in the diffusion model.

This result can be rationalized as follows. In the reaction model nearest-neighbor $AB$ pairs react and are removed from the lattice. The two vacancies thus created are each filled with $A$ or $B$, with equal probability, 0.5, for each species. Thus, the reaction causes nearest-neighbor $AB$ pairs to be replaced by $AA, BB, AB$, or $BA$ with equal probability. Replacement by $BA$ is equivalent to a particle hopping into a nearest-neighbor vacancy if we take $A$ to be a particle and $B$ to be a vacancy. In our diffusion model nearest-neighbor $AB$ pairs are replaced with $AB$ or $BA$ with equal probability. Thus, the reaction model is equivalent to the diffusion model with the addition of the two types of events $AB \rightarrow AA$ and $AB \rightarrow BB$. Now consider a strip of the lattice of height $\Delta z$ parallel to the $x$ axis. On average the number of events $AB \rightarrow AA$ and the number of events $AB \rightarrow BB$

will be the same. We can consider any particular pair of such events to be made up of one $AB \rightarrow AB$ event and one $AB \rightarrow BA$ event plus an exchange $A \leftrightarrow B$ between the two nearest-neighbor pairs. Except for this particle exchange the reaction model is thus *exactly* the same as the diffusion model. Since the exchange in the strip that we are considering occurs in a direction parallel to the $x$ axis, it does not affect the average magnetization $M(z)$, which therefore obeys the diffusion equation with the same diffusion coefficient as in the diffusion model. Since the average magnetization $M(z)$ obeys the same diffusion equation in both the reaction model and the diffusion model, we expect the width of the profile $w_r$ to be identical for the two models. This is confirmed by the results shown in the inset of Fig. 1. Therefore, we conclude that the average concentration profile for the reaction system is simply described by a diffusion equation with a diffusion coefficient $D$ equal to $\lambda^2\Gamma$, where $\lambda$ is the lattice constant and $\Gamma$ is the rate of *reaction* for a nearest-neighbor $AB$ pair.

Another quantity which characterizes the structure of the interface between the two reacting species is the roughness of the interface between the two domains of $A$ and $B$. In order to obtain the roughness of the interface, we make use of the external perimeters of the reactant domains. For the $A$ domain this is defined as the set of all $A$ particles that are connected by nearest-neighbor $A$ particles to $z = -\infty$ and are also connected by nearest-neighbor $B$ particles to $z = +\infty$. The analogous quantity for the $B$ domain gives its external perimeter. The roughness $w_e$ of the interface is then taken to be the root-mean-square position of the particles which constitute the external perimeter. Another way to define the interface is to consider the hull of each of the reactant domains. For the $A$ domain, the hull consists of all the $A$ particles which are connected by nearest-neighbor $A$ particles to $z = -\infty$ and are also connected by next-nearest-neighbor $B$ particles to $z = +\infty$. The external perimeter is more relevant than the hull for the Langmuir-Hinshelwood model that we are considering. This is because all the particles constituting the external perimeter are in a position to react, since they each have at least one nearest-neighbor particle of the other species. This is not the case for the hull.

Since the concentration averaged along the $x$ axis is the same for both reaction and diffusion, it is of interest to determine the fractal dimension of the reaction interface and compare it to the fractal dimension of the diffusion front. The fractal dimension of the external perimeter of the diffusion front has been found to be equal to 4/3 [15].

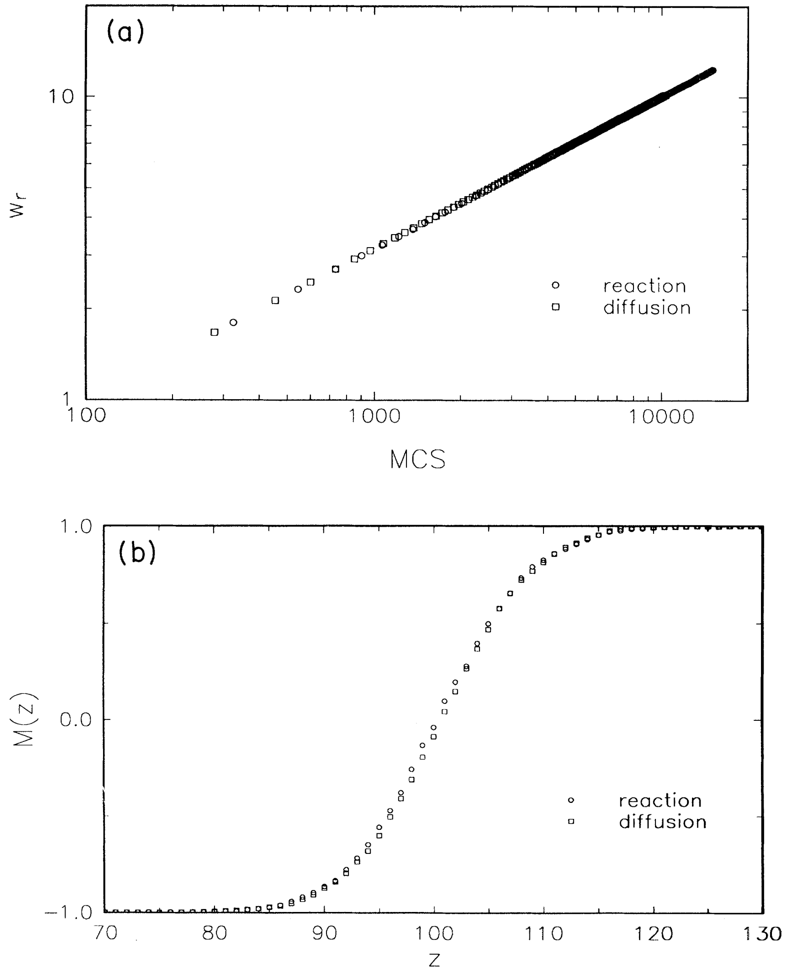

FIG. 1. (a) The dependence of the reactive zone width $w_r$ upon time, measured in Monte Carlo steps per site. Results for both the reaction and the diffusion models are shown. (b) The magnetization profiles $M(z)$ for the reaction and the diffusion models. These models have the same $M(z)$ and the same $w_r$ as may be seen in (a).

Note that the fractal dimension of the external perimeter is different from the fractal dimension of the hull, which is equal to 7/4 [8], i.e., the fractal dimension of the diffusion front is sensitive to the fine details of its definition. As has been pointed out earlier [8], the diffusion front is fractal only on the length scale of its roughness. Thus, the fractal dimension $d$ may be obtained from $Nw_e/L \sim w_e^d$, where $N$ is the number of particles belonging to the external perimeter in a system of width $L$. In Fig. 2 we plot the results of our simulations of the reactive interface and we find that $d$ is equal to $1.33 \pm 0.01$. Therefore, the fractal dimension of the external perimeter of the reaction front is equal to that for the external perimeter of the diffusion front.

It is also useful to compare the fractal dimension of the external perimeter found here with that in a similar reactive lattice-gas model which has been previously investigated [16]. In that model the reaction rate is infinitely higher than the adsorption rate, while in our model the opposite is true. It was found that the fractal dimensions for the hull and the external perimeter are both equal to 1.47. From our simulations the fractal dimension of the hull in our model is also approximately 1.47, although the external perimeter has a fractal dimension of 4/3. This difference can be explained as follows. In the model previously investigated, each vacant site has the same probability of being picked for adsorption. Upon adsorption a particle reacts immediately with any one of the nearest-neighbor particles of the other species with equal probability. Hence a reactant particle at the end of a narrow channel has a probability of reaction (and subsequent removal from the lattice) equal to 1/3 of the reaction probability for a particle at a flat part of the cluster surface, i.e., a particle at the end of a narrow channel has effectively 1/3 of a vacant nearest neighbor. On the other hand, each nearest-neighbor $AB$ pair is picked with equal probability in our model. Hence we expect narrow channels to develop with a greater probability in our simulations. From the definitions of the hull and the external perimeters, we would expect the fractal dimensions of these structures to be different if narrow channels are present at the interface. Thus, the results presented here imply that narrow channels play an important role in the structure of the interface for our model. It is also clear from this example that the mechanistic details of the reactive lattice gas can significantly affect the fractal dimension of the interfacial structure.

Even though the fractal dimension and the average concentration profile of our reaction front are the same as the corresponding quantities in the diffusion front, it is clear that the behavior of these fronts cannot be identical. This is because, in the reaction model, there is a tendency for clusters of like particles to form, since nearest-neighbor pairs of particles of different species are continuously removed form the lattice. Starting with an initially randomly populated lattice, clusters of particles of the same species are expected and observed to form [17]. This is not the case in the diffusion model. Such a positive correlation in the occupation of sites by particles of the same species implies that the clusters of $A$ and clusters of $B$ formed in the reactive zone are larger than those found in the neighborhood of the diffusion front after the same length of time in the simulations. Since the roughness of both fronts can be expected to grow as the size of these clusters, we expect the roughness of the reaction front to increase with time faster than the roughness of the diffusion front.

In Fig. 3 we plot the roughness of the external perimeter for both the diffusion and the reaction models as a function of time in Monte Carlo steps per site. In the case of the diffusion model, $w_e$ scales with time as $t^\beta$, with $\beta$=0.28 ± 0.01. This result is expected from Sapoval, Rosso, and Gouyet's work on the diffusion front [8], although there the roughness is measured by the root-mean-square position of the particles that constitute the hull of the diffusing particles. Even though the fractal dimension of the hull is different from that of the external perimeter, it is apparent that their roughness scales with time with the same exponent. From the definitions of the external perimeter and the hull, it is also clear that the external perimeter is really a subset of the hull. If the spatial distribution within the hull of particles that constitute the external perimeter is invariant with time, then the roughness of the hull and the external perimeter will both scale with time with the same value of $\beta$. Our results suggest that this is indeed the case.

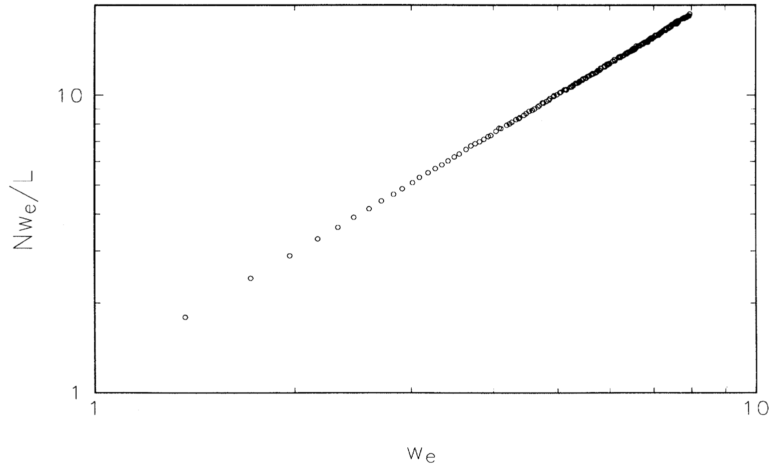

FIG. 2. The dependence of $\frac{Nw_e}{L}$ upon $w_e$. The quantity $\frac{Nw_e}{L}$ is a measure of the external perimeter length in a section of the lattice of width $w_e$ along the $x$ axis. The lattice has a width of $L$ in the $x$ direction. This plot shows that the fractal dimension of the external perimeter for reaction is identical to that for diffusion.

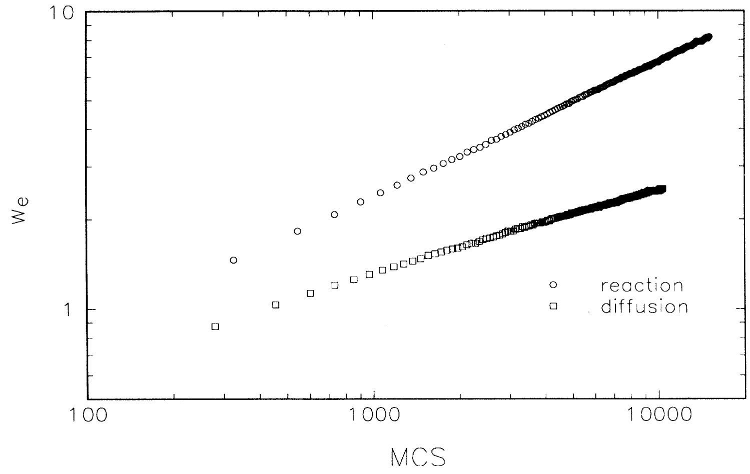

FIG. 3. The roughness of the external perimeter $w_e$ is plotted as a function of time for both reaction and diffusion. It is clear that the roughness increases more rapidly with time in our reaction model than in diffusion.

The roughness of the external perimeter in the case of the reaction model shows a much larger exponent, $\beta$=0.455 ± 0.005, than the value expected and obtained in the diffusive case; cf. Fig. 3. This value of $\beta$ is also larger than the roughening exponent obtained for the interface in a Ising model. There $\beta$ was found to be equal to 1/4 below the critical temperature, and at the critical temperature a value of approximately 0.47 was obtained. We have previously investigated the interface roughness in a slightly different model of a lattice-gas reaction [10]. There the reaction rate was set to be infinitely higher than the adsorption rate such that in addition to $A$ and $B$ particles on the lattice, the lattice also contains vacant sites in the reactive zone. For that model, an effective surface tension can be obtained by including attractive interactions between like lattice-gas particles. When there are no attractive interactions between like lattice-gas particles, as is the case considered here, the roughness was found to scale as $t^{1/2}$. Therefore, the scaling of the interface roughness with time is apparently dependent upon whether the reaction rate is infinitely higher than the adsorption rate or vice versa.

In these reactive lattice gases, the reaction rate per unit area of the lattice decreases with time if we begin with an initially randomly populated lattice. This is because clusters of like particles grow and reaction can only occur at the periphery of these particles. It has been observed that such "poisoning" occurs rather slowly with time, and the reaction rate scales with time as $t^{-\gamma}$, where the exponent $\gamma$ is rather small. One would expect that this slow poisoning is related to the observation of the large (i.e., close to 1/2) roughening exponent $\beta$ in these models, an issue we are pursuing further.

The diffusion front has been shown to be geometrically similar to the surface of a percolation cluster [8]. Consider a particle which is at some distance from the average position of the front. There is a correlation length corresponding to the average density of particles $\rho$ at that position. If this correlation length $\xi$ is less than or equal to the distance of the particle from the average front position $z_f$, then the particle is likely to be part of the front, i.e., $w_e + K\xi(z_f \pm w_e)$, where $K$ is a constant of order unity. Using an argument by Sapoval, Rosso, and Gouyet [8], it can be seen that the roughness scales with time as $w_e \sim t^{\nu/2(1+\nu)}$. In two dimensions $\nu$, which is the exponent for the scaling of the correlation length with particle density $\xi \sim (\rho - \rho_c)^{-\nu}$, is equal to 4/3, so that we would expect the roughening exponent $\beta$ to be equal to 2/7. We find that this is the case for both the external perimeter and the hull of the diffusion front, but, as we have seen, it is not true for the reaction front. We only have data for the external perimeter, but the hull would also be expected to have a roughening exponent $\beta$ equal to approximately 0.455 [17]. It is probably not the case that $\nu$ is different for the reaction model. Rather the argument used to arrive at the equation $w_e = K\xi(z_f \pm w_e)$ and thus $w_e \sim t^{\nu/2(1+\nu)}$ is probably not valid in the reaction model where there is a positive correlation between the occupancy of sites by particles of the same species.

## IV. CONCLUSIONS

We have investigated the structure of an initially flat interface between two reactant domains $A$ and $B$ in a square lattice-gas model of a Langmuir-Hinshelwood reaction. Reaction occurs between nearest-neighbor $AB$ pairs. Adsorption occurs immediately into any site vacated by reacting particles with equal probability of $A$ and $B$. We compare the particle density profile in the reaction model with that in a diffusion model. In the latter, we simply regard $A$ as diffusing particles and $B$ as vacancies on the lattice. An argument is provided to show that the particle density profile in the reaction model is exactly the same as if species $A$ were diffusing on a lattice and species $B$ were vacancies. Particle-density profiles obtained from the simulations show this to be the case.

We also obtained the fractal dimension of the external perimeter of the reaction front. This is equal to 1.33 ± 0.01 and is the same as that of the external perimeter of the diffusion front so that the reaction front and the diffusion front are geometrically similar. It is, however, different from the fractal dimension of the external perimeter in a slightly different reaction model. We show that the microscopic details of the model can account for this.

Even though the reaction front and the diffusion front are geometrically similar, there is a difference between the reaction model and the diffusion model. This is because a positive correlation exists in the site occupancy between particles of the same species in the former. As a consequence of this correlation, we expect the clusters formed in the reaction zone to grow faster than the clusters formed in the neighborhood of the diffusion front. Thus, the reaction front roughens faster. The exponent for this roughening is found to be 0.455 ± 0.005. We speculate that the large value of this roughening exponent is related to the slow poisoning which occurs in this and other similar reactive lattice-gas models.

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