

Monte Carlo Simulation of Surface Adsorption–Diffusion–Reaction Kinetics

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Received: September 10, 1998; In Final Form: January 13, 1999

A surface adsorption–diffusion–reaction model is proposed and tested by Monte Carlo simulations. The solvent shell effect is considered as a geometric constraint and the Langmuir adsorption mechanism is also incorporated. An anomalous power law of $t^{1/2}$ is obtained for the amount of material removed from the surface vs time. The result agrees well with etching experiments of SAM on a silica surface. We conclude that the unusual power law results from an interplay of vacancy growth and fusion at the surface.

Introduction

Reaction kinetics in confined domains often exhibit anomalous behavior.^{1–4} In this paper, we present a new model resulting in nonclassical kinetics in an elementary $A + B \rightarrow 0$ reaction at a surface/interface with B as adsorbent. Chemistry at a surface or interface is important not only to some traditional applications, such as chromatography and electrophoresis, but also to surface adhesion and to microelectronic structures in silicon wafers.^{5–12} Often the system encountered is not a purely two-dimensional system and the material at the surface is not necessarily confined to the surface, rather it is deposited or adsorbed from the bulk and it can also desorb back into the bulk. Under our simple condition of steady replacement (from solution) of surface B (etching) particles and a great preponderance of surface A (the monolayer) particles, one would expect a time-constant etching process, i.e., a removal of A particles that is linear in time. We find the story to be more complex.

We consider the following example. A basic alcohol solution is known to remove the surface Si–O–Si bonding, e.g., the self-assembled monolayer,¹³ and, therefore, increase the number of surface silanol functional groups, i.e., the surface negative charges. The etching process of self-assembled monolayers has been studied experimentally using a SHG (second harmonic generation) technique.^{14,15} An anomalous algebraic power law of $t^{1/2}$ was observed for the etching, i.e., for the total self-assembled monolayer mass removal. To explain this unusual power law, we proposed a surface adsorption–diffusion–reaction model. We performed preliminary Monte Carlo simulations which agreed well with the experimental kinetics at the surface. In this paper, more extensive computer simulations were performed to determine the origin of this anomalous power law.

Model and Simulation

Often, in the study of multibody chemical reactions kinetics, exact theoretical solutions are difficult, perhaps impossible, to attain. Computer simulation of more complex dynamics becomes a necessary tool for investigating the phenomena of reaction kinetics. Our model is a surface adsorption–diffusion–reaction model. In this model, the reactant does not react with the surface species directly (probably due to steric hindrance), rather, the reactant will have to adsorb onto the surface first and then diffuse to the reaction site. For simplicity, we adopt the

Langmuir adsorption model which assumes that the interaction of adsorbent molecules is the same among all the adsorbent neighbors. The free energy of the adsorption is related to the species solvation energy in the bulk and at the surface. In solution adsorption, when a molecule lands on the surface from the bulk, it has to break up the solvent shell and become solvated at the surface. The energy difference of the above process makes up the free energy in the Langmuir adsorption. Suppose that there are two different domains of sites at the surface, labeled S1 and S2, respectively, then the adsorption on these two domains may be different because the surface solvation could be very different. In our simulations, we imposed a solvent shell for each B landing onto the surface. When B is on the surface, the case of a B landing with no A in the neighborhood (so that B lands in an empty domain) will be quite different from the case where B has an A as a nearest neighbor. This translates into the solvation energy difference. Therefore, we can bias the landing of B by geometrical constraints. We draw an exclusion area around A. It is a crude way of simulating Langmuir adsorption free energy, but it catches the physics of the process.

In our previous simulation,¹⁵ we showed that when the solvent shell effect is considered as a geometric constraint and the Langmuir adsorption mechanism is incorporated, an anomalous power law of $t^{1/2}$ is obtained for the amount of material removed from the surface vs time. The simulation usually starts with a fixed amount of reactant A particles, randomly landed onto a 1024×1024 lattice. B particles are landed onto vacant and unshielded sites. We only consider the early stage of Langmuir adsorption, i.e., the stage where the adsorbent population at the surface is linearly dependent on the number of surface empty sites. Technically, we maintain the ratio between the numbers of empty sites and that of B particles at the surface as a fixed constant during the computer simulation. We tried different initial coverages of A and different excluded volume conditions. These excluded volumes express the shielding of potential B landing sites by the adjacent bulky A particles (umbrella type shielding). The A particle never moves; only B is doing the random walking. If B encounters an A in a move, both are removed. After all the B particles are moved once in a time step, the ratio between the number of B particles and number of empty sites is examined again and lost B particles are compensated for by landing randomly more B particles so as to maintain this ratio. A finite lifetime is assigned for each B particle (this is for the desorption process). We monitor the total number of A particles removed as a function of time steps.

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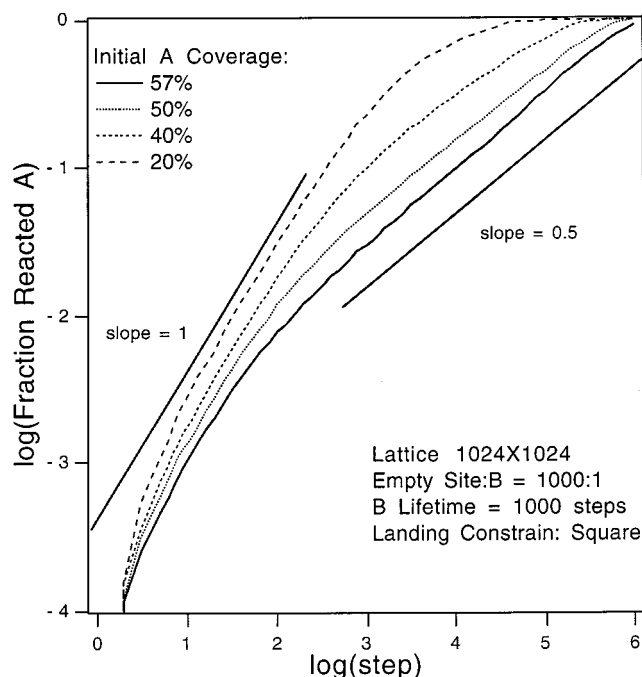


Figure 1. Simulation results with a square-shaped landing constraint with different initial coverages of A. Both 50% and 57% data show a power law dependence with an exponent of 0.5–0.6.

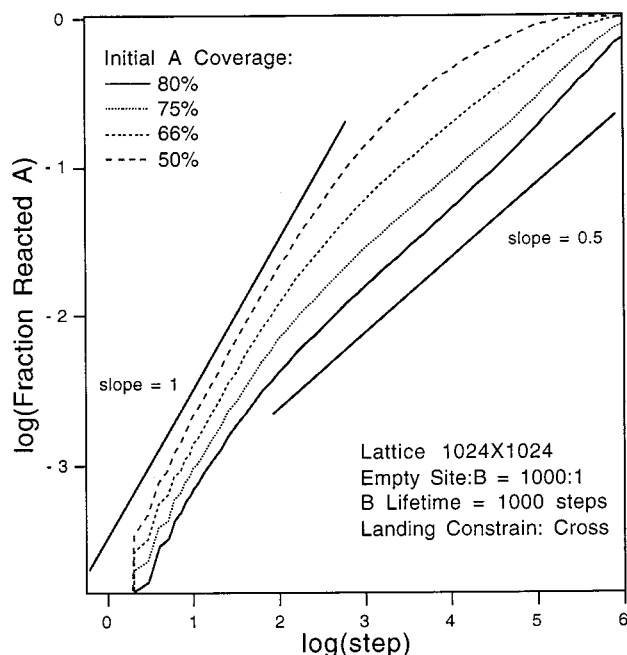


Figure 2. Simulation results with a cross-shaped landing constraint with different initial coverages of A. Both 75% and 80% data show a power law dependence with an exponent of 0.5–0.6.

Result

Figure 1 shows simulation results with a “square-landing” constraint (first and second nearest-neighbor exclusion, also known as “hard square model”),¹⁶ with different initial coverage of A. We see a power law of $1/2$ dependence on time when the initial A coverage is approaching a geometrical limit, i.e., 57% surface coverage (where further B landing becomes impossible). Figure 2 shows simulation results for “cross forbidden” landing (nearest-neighbor exclusion). The same asymptotic 0.5 power law now appears starting at a higher initial coverage of A. Again, this asymptotic 0.5 power law seems to coincide with the

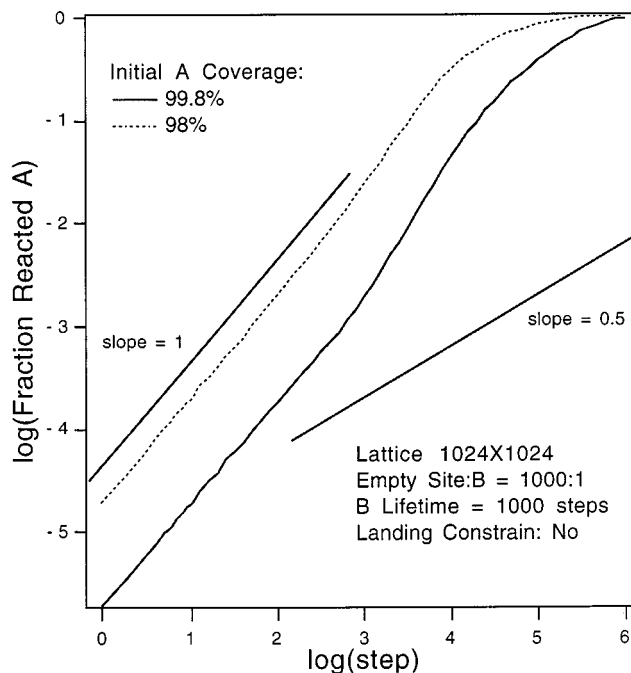


Figure 3. Simulation results with no landing constraint. The initial coverage of A can be as high as 99.8%.

geometrical limit of cross-excluded constraint, about 80%. We also performed simulations without a landing constraint. In this case, the initial coverage of A can be pushed to a high value. From our simulations, even for an initial coverage of 99.8% it is inconclusive if we see a power law 0.5 at late time (see Figure 3). From the comparison of these results, it is thus clear that the landing constraints play a vital role in the surface adsorption–diffusion–reaction kinetics. The existence of surface landing constraints always slows down the reaction rate, as can be seen from Figures 1–3.

To understand the origin of the asymptotic power law kinetics, it will be interesting to see the surface configuration during the simulation.⁴ Snapshots of the surface were taken to check the surface topography at different times. The patterns for a simulation with a square-landing constraint are shown in Figure 4. The result is for a 256×256 square lattice with a 57% initial coverage of A, and the ratio of B to empty sites is 1:1000. From the patterns at different times we conclude that as time progresses the different size pores grow larger and merge; the pores with the larger sizes grow faster and therefore dominate the reaction kinetics, a mechanism that can be described as “hole growth and fusion”. The surface configuration at step = 1000 ($\sim 1\%$ A removed) already shows some degrees of “hole fusion”, while the configuration at step = 10000 ($\sim 10\%$ A removed) simply indicates a pore growth and merger. It is easy to understand that the larger pore will grow fast and therefore dominate the reaction kinetics, because the adsorption (relanding of B unto surface after each time step) will favor the pores with larger area if the relanding is a random process. Therefore, after the initial reaction steps, a pore emerging with a larger area will have more B accumulated in the pore. This accumulation may cause the kinetics to slow; it will be necessary for B to diffuse a longer distance before a reaction occurs if it is landed into a larger pore. It is natural to think that this is similar to a diffusion model where B lands in the middle of the pore, and diffuses to the wall of the pore. The $1/2$ power law is also intriguing; is it possible that this is just a two-dimensional diffusion where B diffuses toward a wall? The result in Figures 3 and 5 negates this possibility. The adsorption–diffusion–

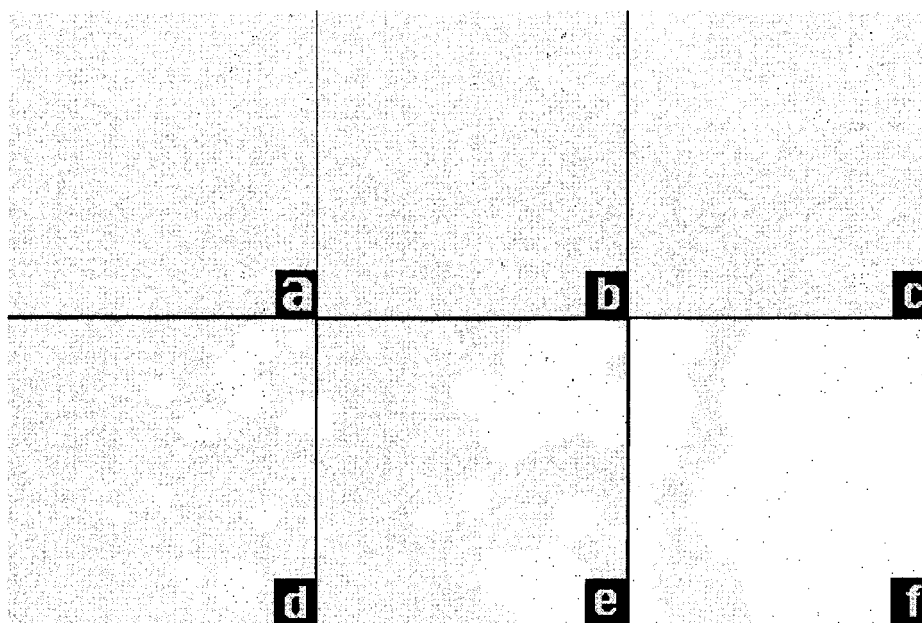


Figure 4. Patterns on the surface generated from simulations at different time steps. Lattice size 256×256 . Initial surface coverage of A is 57%. The B landing constraint is a square landing constraint (second nearest neighbor forbidden). The ratio of empty sites to B is 1000:1. Patterns labeled a–f are taken from 10, 100, 1000, 10000, 100000, and 1000000 time steps, respectively (white, empty sites; gray, A; dark, B).

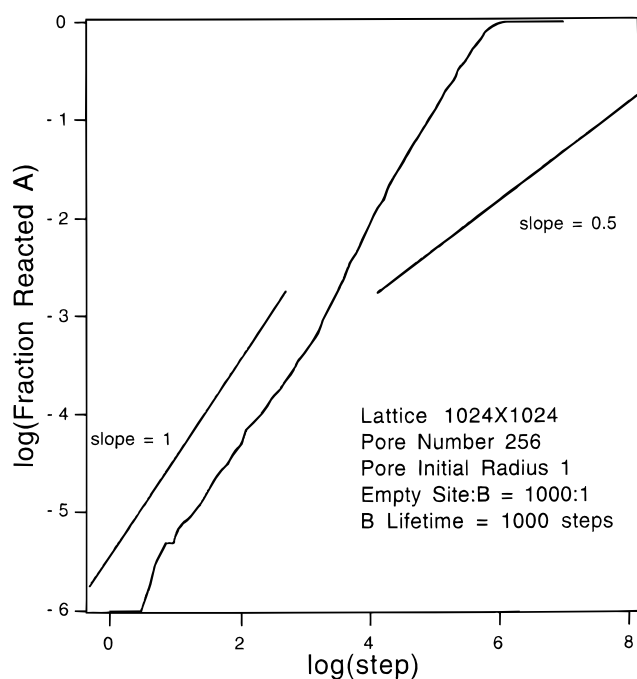


Figure 5. Simulation for “many-pore” superlattice with initial 100% surface coverage of A.

reaction model with no landing constraint will give a power law of more than 1, a much faster reaction kinetics (see below).

To understand the details of “pore growth and fusion” behavior, we performed several more computer simulations. We started with a single pore simulation. We first create a single pore (size = 25) at the center of a two-dimensional lattice while the rest of the lattice sites are filled with A. A number of particles B (proportional to the number of surface empty sites) are randomly deposited inside the pore and perform random walks, the same way as in the previous simulations. The A's completely fill the lattice outside the pore. The landing of B is as random as before. We consistently get a power law about 1.1 with different lifetimes of B, which is significantly different from the power 0.5 we obtained from the previous simulations.

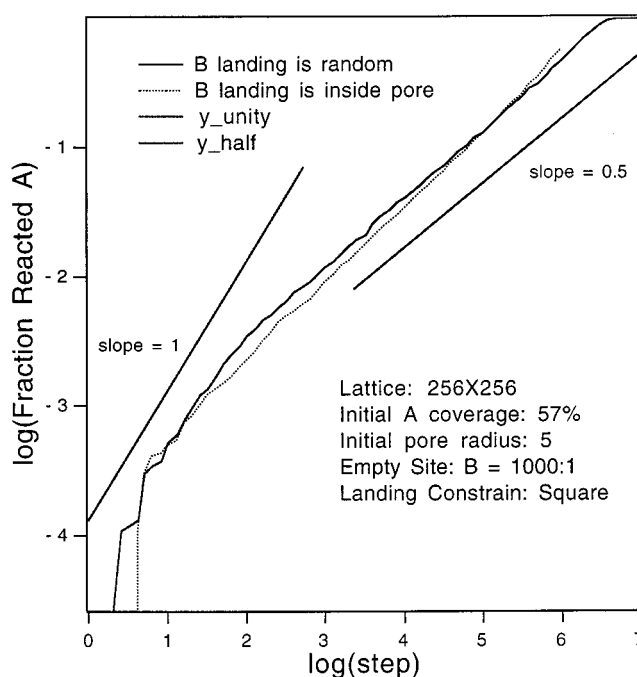


Figure 6. Simulation results for a roughly 57% initial A coverage, with one artificial pore.

It thus appears that a many-pore model or a very rough pore boundary is required for the $t^{1/2}$ power (in Figure 4, we can see a lot of tiny pores). Some “many pores” superlattice simulations were also performed. We artificially planted 256 pores on the lattice, distributed evenly (not randomly). The areas outside of the small pores are filled with A. The B particles are randomly deposited into the small pores. We plot $\log(\% \text{ reacted A})$ vs $\log t$ and get a slope of 1.1–1.2 (Figure 5). This result is consistent with the “single-pore” simulations. The pattern shows that the pores have a near circular shape throughout the simulation, until just before merging. In fact, it turns out that the “many pores” superlattice simulation gives just a better statistics for the single-pore simulation. Therefore, it is concluded that a rough boundary of pores is needed in order to

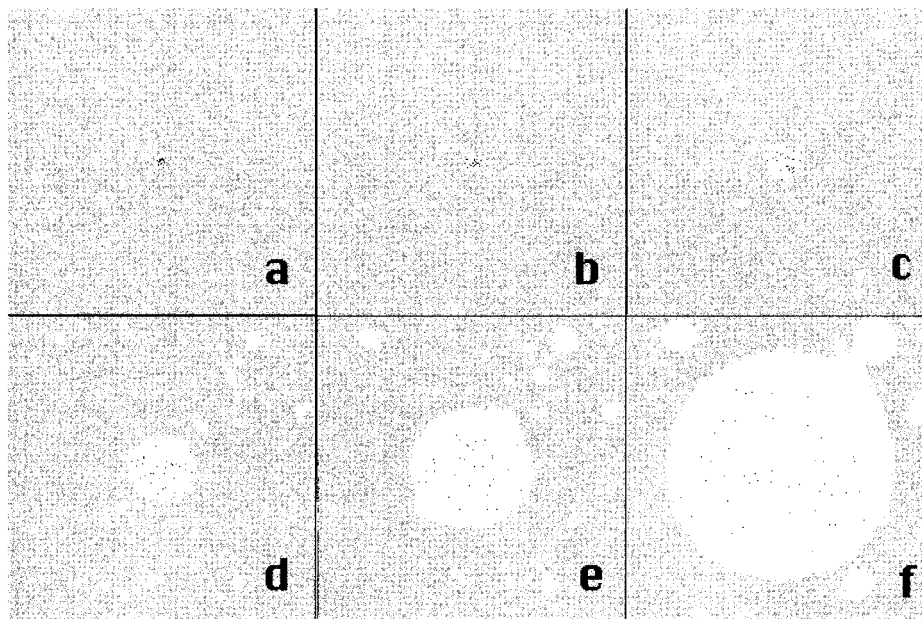


Figure 7. Patterns from simulations where one artificial pore is created. Lattice size 256×256 . Initial surface coverage of A is 57%. The B landing constraint is a square landing constraint (second nearest neighbor forbidden). The ratio of empty sites to B is 1000:1. Patterns labeled a–f are taken from 10, 100, 1000, 10000, 100000, and 1000000 time steps, respectively (white, empty sites; gray, A; dark B).

obtain the asymptotic power law kinetics. From Figure 4, it seems that the random 57% initial coverage of A automatically gives rise to the roughened pore boundary during the simulation. Is this the origin for the observed power law kinetics?

Figure 6 shows the result of a simulation where we started with 57% of A on the lattice and picked (dig) a circular area (hole) and remove all the A particles from the hole (the total coverage thus is slightly smaller than 57% of A). In this case, most B will mainly be deposited into the large hole we dig and this hole grows bigger and faster. This is similar to the “single-pore” simulation we did earlier, except that now the area outside of the pore is not completely filled. Here we observe a power law dependence of close to 0.5 (Figure 6). We also look at the patterns at different time steps (Figure 7) which are remarkably similar to the original “hole growth and merging” patterns (Figure 4) except the artificial pore grows much faster and larger. In fact, the time dependence in the two cases (Figures 1 and 6) is almost the same, with the same power law exponents. This indicates that the *roughness* of the boundary and the *merging of small pores* have an important effect on the power law.

What if we force all the B to land inside the pore? In the next simulation, we again created a hole on the same lattice as above. In this case, we forced all the B's to land inside the artificial hole (as opposed to the previous random deposition). This differs from the previous simulation in that the kinetics are completely dominated by the reaction at the artificial pore boundary. A slope of 0.586 is obtained which is close to 0.5 (Figure 6). Different simulations with different initial coverages and landing constraints show consistently a slope between 0.5 and 0.6. It should be noted that the condition for this set of simulation is the same as that of the “single-pore” simulation in Figure 5, except that on the outside of the pore the A coverage is only 57%. We also performed simulations using cross-exclusion constraints for initial A coverage of 80% and obtained similar results. Therefore the pore boundary is really rough and many pores with various smaller sizes are adjacent to the larger artificial one. The results support the conclusion that the *roughness* of the boundary and the *merging of small pores* are the controlling factors on the power law kinetics. We shall also note that the observed unusual $t^{1/2}$ dependence seems to become

apparent only when the initial surface coverage is approaching geometrical limits.

Summary

We proposed a two-dimensional adsorption–reaction–diffusion model for the etching of SAM from the silica–water interface. This model considers different free energy constraints for the adsorption process. We performed Monte Carlo simulations based on a number of variants of this model. There is good agreement between our etching experiment and specific simulation results. We also show that the unusual $t^{1/2}$ dependence does not result from single smooth pore growth. From these computer experiments we conclude that in order to obtain the anomalous power law a continuous hole growth and fusion mechanism is necessary.

Acknowledgment. We acknowledge support from the National Science Foundation, grant DMR 9410709.

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