

The formation of surfaces by diffusion limited annihilation

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Computer simulations have been carried out in two and three dimensions to explore the formation of surfaces by diffusion limited annihilation of an initially smooth surface by mobile particles. From simulations carried out on two-dimensional strips of width l lattice units we find that the asymptotic variance in the surface height (ξ) scales with l according to $\xi \sim [\ln(l)]^{1/2}$. For three-dimensional systems with a square cross section of size $l \times l$ lattice units we find that ξ quickly reaches a limiting value which is essentially independent of l ($\xi \sim l^0$). A variety of two-dimensional simulations were also carried out for other geometries. The results of these simulations indicate that diffusion limited annihilation processes cannot be used to produce sharply defined grooves by etching through an inert mask.

INTRODUCTION

Diffusion limited processes are of considerable scientific interest and practical importance. During recent years a wide variety of such processes including aggregations,^{1,2} chemical reactions,³⁻⁶ particle coalescence,⁷ trapping by stationary sinks,^{8,9} and phase separation processes^{10,11} have been studied theoretically, by computer simulations and experimentally. One area which has received much attention is the formation of fractal structures¹² by a variety of nonequilibrium growth and aggregation processes.^{1,2,13-15} The reverse process of diffusion limited annihilation in which material is removed by particles following random walk trajectories has been studied much less. One reason for this is that such processes are expected to lead to "uninteresting" nonfractal surfaces. However, material removal is important in many areas of technology such as electropolishing, corrosion, and etching. Under some circumstances these processes may be diffusion limited. It is also of some fundamental significance to know just how smooth a surface formed by diffusion limited processes may be.

In this paper we explore a simple model for material removal in which particles are started, one at a time, on random walk trajectories (on a lattice) a long distance from the surface. If the randomly walking particle steps onto an occupied lattice site that site and the particle are annihilated and a new particle trajectory is started. We show that a nontrivial scaling relationship exists between the variance in the surface height and the lattice width for simulations carried out on a two-dimensional lattice with periodic boundary conditions in the lateral direction. For simulations carried out on cubic lattices (also with periodic boundary conditions in the lateral directions) we find that the variance in the surface height is independent of lattice size in the long time limit.

Our work was motivated in part by the recent discovery¹⁶⁻¹⁸ that even very simple growth models (such as the Eden model^{1,2,19,20} and ballistic deposition model^{1,2}) which generate structures with compact (nonfractal) interiors can lead to surfaces which have a complex geometry. In particular the variance of the surface height (ξ) has been found to

scale with the strip width (l) and mean deposit height (h) in two-dimensional simulations according to

$$\xi(h) \sim l^\alpha f(h/l^\beta) \quad (1)$$

for both the Eden and ballistic deposition models. Here α and β are exponents which have values close to 0.5 and 1.6 for both models.^{15,17,20,21} A theoretical analysis indicates that in two-dimensional systems, $\alpha = 0.5$ and $\beta = 3/2$.²² The scaling function $f(x)$ in Eq. (1) behaves according to $f(x) \rightarrow \text{constant}$ for $x \rightarrow \infty$ and $f(x) \sim x^{\alpha/\beta}$ for $x \rightarrow 0$.

We were also interested in using this model to explore if diffusion limited etching processes could be used to produce specified surface shapes by etching through inert masks which could be useful for fabricating electronic and optical devices. Our results indicate that diffusion limited processes are not suitable for the production of deep grooves with sharp corners. This is not surprising in view of the main conclusion of our other simulations which indicate that diffusion limited annihilation leads to very smooth surfaces. It follows that etching processes cannot rely upon diffusion for mass transport of active ingredients if sharp feature definition is desired.

A quite different diffusion limited decay model has been investigated by Muthukumar, Banavar, and Willemsen²³; in this model the random walker is not destroyed on contact with an occupied surface site. Rather, the random walk is continued and every site contacted is removed. This model does not represent the sort of process investigated here. The surfaces produced by this model are very rough and probably have a fractal geometry.

SIMULATIONS

The simulation of diffusion limited annihilation closely resembles earlier simulations of diffusion limited deposition onto a surface.²⁴ Figure 1 represents an early stage in a small two-dimensional simulation. A particle is started off a few lattice units higher than the highest occupied surface site and undergoes a random walk on a square lattice. If the random walk eventually causes the particle to step onto an occupied

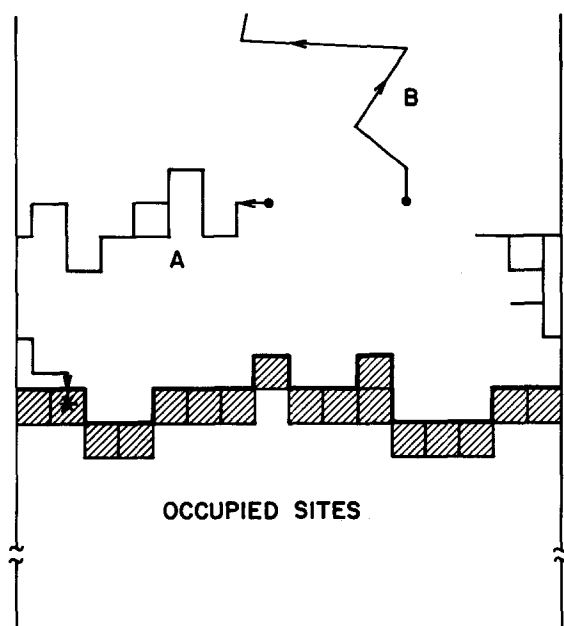


FIG. 1. Schematic representation of a small scale two-dimensional simulation of diffusion limited annihilation. Trajectory A eventually moves the mobile particle onto an occupied surface site (shaded) at which point the particle and the lattice site are removed. This random walk trajectory illustrates the periodic boundary conditions used in our model. Trajectory B moves away from the surface and long off-lattice steps are permitted. This trajectory eventually moves the particle a long way from the surface and the trajectory is terminated. The simulation is carried out on a strip of width l (in this case 16) lattice units.

surface site (the shaded sites in the figure) both the particle and the surface site are removed and any newly formed occupied surface sites are identified. If the particle moves to a height greater than a few lattice units higher than the highest occupied site it is allowed to move off the lattice and take larger steps to improve the efficiency of the simulation. However, the step size is restricted so that the particle cannot move to within a few lattice units from the surface by means of an off-lattice jump. If the particle eventually moves a long distance from the surface [to a height which is more than 100 lattice units from the highest occupied site or more than 500 ξ above the highest occupied site; (whichever is greater)] the trajectory is stopped and a new trajectory is started to reduce computer time requirements. The procedure outlined above is repeated many times (typically several million times in our simulations). Since the surface remains relatively smooth, the process can be continued indefinitely using a finite lattice by moving the surface on the lattice as the simulation proceeds. The methods used to improve the efficiency of the program (mainly allowing long off-lattice jumps when the particle is far from the surface) are similar to those used to improve the efficiency of diffusion limited aggregation simulations and are discussed in more detail elsewhere.^{25,26} In all of our simulations, periodic boundary conditions are used in the lateral direction. Trajectory A in Fig. 1 illustrates this feature of our models.

The three-dimensional model is an obvious extension of the two-dimensional model. In this case, the simulation is carried out on an $l \times l \times h$ lattice with periodic boundary conditions in the x and y directions.

TABLE I. Dependence of the variance of the surface height (ξ) on the strip width l in the limit $\bar{h} \gg l$. The uncertainties are 95% confidence limits (≈ 2 standard deviations).

l	ξ
16	0.7212 ± 0.0006
32	0.8039 ± 0.0010
64	0.883 ± 0.002
128	0.954 ± 0.005
256	1.025 ± 0.005
512	1.088 ± 0.005
1024	1.142 ± 0.015

In Fig. 1 the occupied surface sites are shaded. The occupied surface sites consist of all of the occupied sites with unoccupied nearest neighbors. After each l site has been removed (or after each l^2 site has been removed in the three-dimensional simulations) the mean surface height (\bar{h}) given by

$$\bar{h} = \left(\sum_{i=1}^N h_i \right) / N \quad (2)$$

is determined. Here, h_i is the height of the i th occupied surface site below the original surface and N is the number of such sites. The variance of the surface height (ξ) given by

$$\xi = \left[\sum_{i=1}^N (h_i - \bar{h})^2 \right]^{1/2} \quad (3)$$

is also measured.

RESULTS

The dependence of surface thickness on lattice size

Simulations were carried out on strips of width 16–1024 lattice units. The number of sites removed varied from 8×10^6 for the smaller strip widths to about 4×10^7 for $l = 512$ and 1024. The variance of the surface height reaches a limiting value quite quickly as the material loss process continues and the dependence of ξ on l was determined well after the limiting value had been reached.

Our results are shown in Table I and Fig. 2. Initially, we plotted $\ln(\xi)$ vs $\ln(l)$ but the resulting plots were quite noticeably curved. Figure 2 shows the dependence of $\ln(\xi)$ on

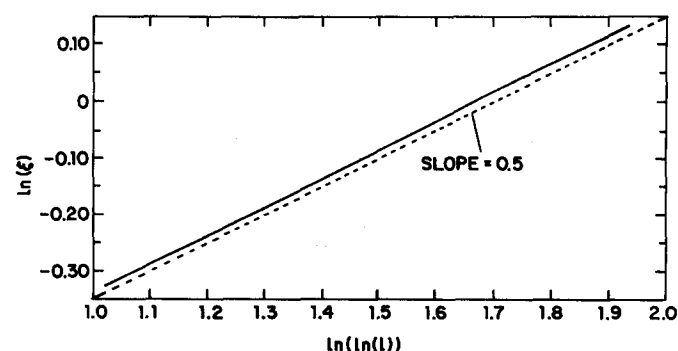


FIG. 2. Dependence of the variance of the surface height (ξ) on the strip width l for two-dimensional (square lattice) diffusion limited annihilation in the long time ($\bar{h} \gg l$) limit.

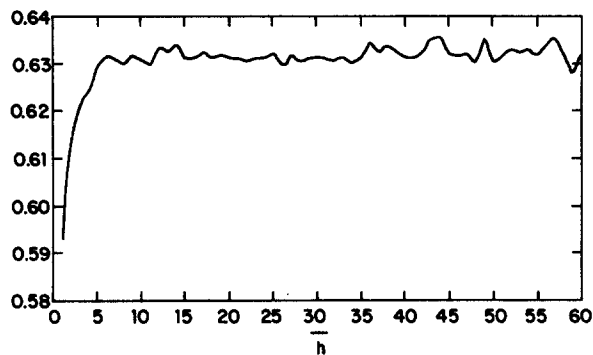


FIG. 3. Dependence of the variance in the surface height on the mean height (\bar{h}) of material removed in a three-dimensional simulation of diffusion limited annihilation on a $256 \times 256 \times h$ lattice.

$\ln[\ln(l)]$. A least-squares fit to the data points in this plot gives a slope of 0.5046 ± 0.0026 where the quoted uncertainty is one standard error. These results strongly suggest that $\xi \sim [\ln(l)]^{1/2}$ for two-dimensional diffusion limited annihilation.

Similarly, simulations were carried out in three dimensions starting with smooth surfaces with an area of $l \times l$ lattice units ($l = 16, 32, 64, 128, \text{ and } 256$). The number of sites removed varied from 3×10^6 for $l = 16$ to 10^7 for $l = 256$. In three dimensions the limiting value for ξ is reached very quickly (Fig. 3). Table II shows how the limiting value for ξ depends on the surface area ($l \times l$). The results shown in this table indicate that ξ has very little dependence of l and are consistent with a limiting relationship of the form

$$\xi \sim l^0. \quad (4)$$

The dependence of surface thickness on the depth of material removed

Figure 3 shows how the surface thickness or variance (ξ) depends on the depth of material removed in a $3d$ simulation. In two dimensions the approach of ξ to its limiting value is much more gradual. In order to investigate this behavior for two-dimensional systems in more detail, the diffusion limited annihilation process was continued until \bar{h} had reached a value of l for $l = 32, 64, 128, 256, 512, \text{ and } 1024$ or until \bar{h} had reached a value of 256 for $l = 2048, 4096, \text{ and } 8192$. A number of simulations varying from 4000 for $l = 32$ to about 25 for $l > 1024$ were averaged to improve the statistics. Figure 4 shows some of the results obtained from these simulations. The results shown in Fig. 4 for the largest strip

TABLE II. Dependence of the variance of the surface height (ξ) on the lattice size ($l \times l \times h$) for three-dimensional simulations of diffusion limited annihilation. The values given for ξ are the long time (large h) limiting values and the uncertainties are 95% confidence limits.

l	ξ
16	0.6161 ± 0.0007
32	0.6253 ± 0.0008
64	0.6296 ± 0.0007
128	0.6310 ± 0.0006
256	0.6319 ± 0.0005

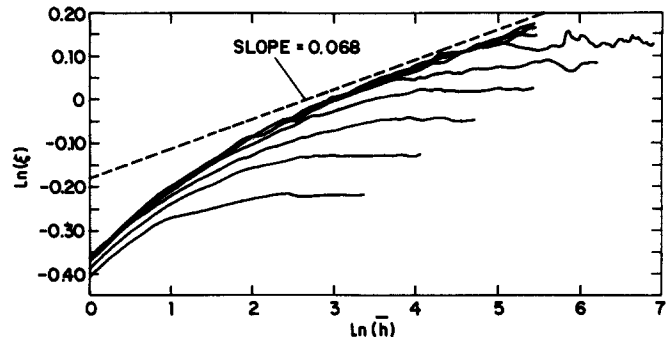
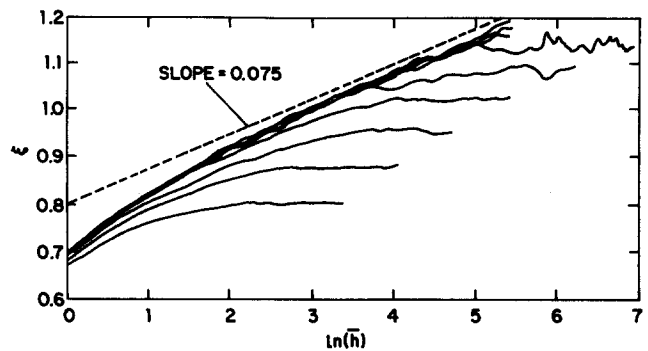


FIG. 4. Dependence of the thickness of the surface (ξ) on the mean surface height removed (\bar{h}) from two-dimensional simulations of diffusion limited annihilation on a square lattice with a width of 32, 64, 128, 256, 512, 1020, 2048, 4096, and 8192 lattice units. (a) shows the dependence of ξ on $\ln(\bar{h})$ and (b) shows the dependence of $\ln \xi$ on $\ln \bar{h}$.

widths suggest that after an initial steep increase a regime may exist where ξ increases with a small power of \bar{h} or more probably with a power of $\ln(\bar{h})$ as shown in Fig. 4(a). We have tried various ways of scaling the data shown in Fig. 4 onto a single curve but have not so far been successful.

Other geometries

A series of two-dimensional simulations have been carried out to explore the possibility of using diffusion limited annihilation to produce sharply defined structures and to investigate other aspects of diffusion limited annihilation. These simulations have been carried out in two dimensions but we believe that the results can help us to anticipate what may happen in similar three-dimensional systems which would correspond more closely to processes of practical importance.

Diffusion limited annihilation has been investigated for this purpose using a variety of different geometries. Some of our results are shown in Fig. 5. To obtain Fig. 5(a) part of the surface was covered by an inert mask which is represented by a single layer of lattice sites. If a random walker steps onto one of these sites it is returned to the site which it previously occupied. In this case the inert site occupies alternating bands which are 32 lattice sites wide. In the early stages of the material removal process grooves are created in the surface but they do not have sharp corners and the inert mask is soon undercut. Before too long the mask is completely separated from the receding surface which rapidly becomes smoother.

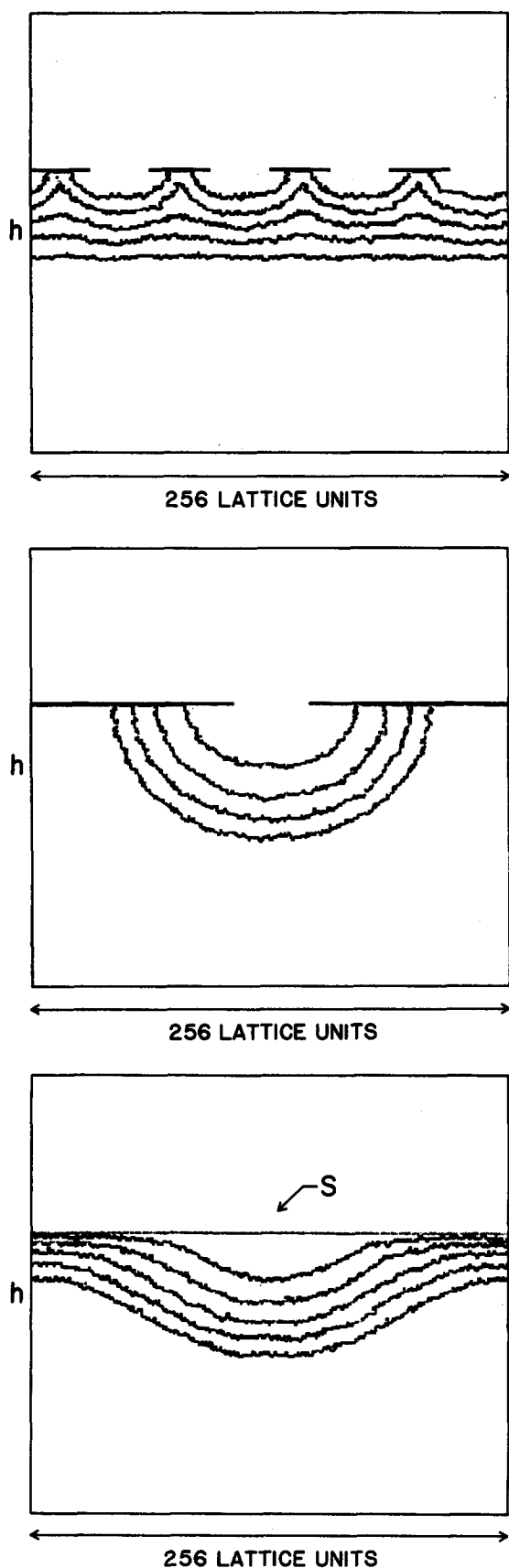


FIG. 5. This figure shows diffusion limited surface annihilation for several different geometries. In (a), a single layer of "inert" lattice sites have been placed on top of the original surface. These inert sites form a broken line with gaps and filled regions which are both 32 lattice sites long. In (b) the surface is completely protected except for a gap 40 lattice units wide and in (c) the surface is unprotected but all of the random walkers start off at a single lattice site indicated by the letter S.

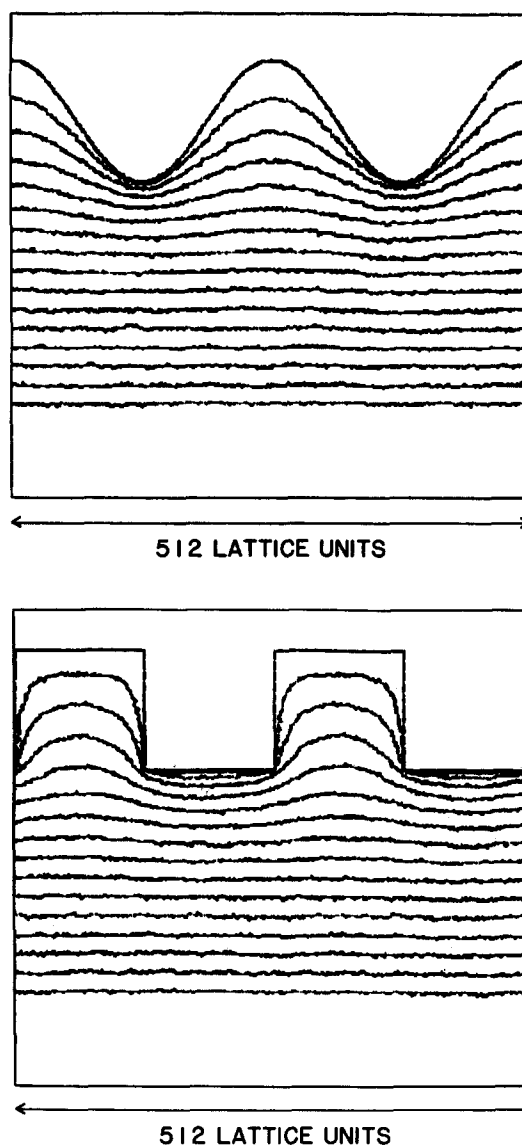


FIG. 6. This figure illustrates the decay of an initially rough surface. In (a) the initial profile is sinusoidal with a wavelength of 256 lattice units and an amplitude of 64 lattice units. In (b) the original surface is represented by a square wave. Each step in the surface of the square wave has a length of 128 lattice units.

In Fig. 5(b) the surface is covered by an inert layer except for a gap which is 40 lattice units wide. Again, the inert mask is severely undercut. This simulation can be taken to represent the erosion of a surface which is covered by a protective coating which contains defects. In Fig. 5(c) the surface is not covered by inert sites at any position. However, all of the random walkers are started at a single site (indicated by the letter S in the figure). In this case a broad shallow hole is removed from the original surface.

The two-dimensional model has also been used to investigate how an initially rough surface (represented by a sinusoidal or square wave profile) becomes smoother. Some qualitative results are shown in Fig. 6. It is apparent from Fig. 6 that the surfaces become smooth very rapidly and that surface roughness with an amplitude of δh is almost completely removed after the average surface height has been reduced by about $2\delta h$. In order to investigate this process in a

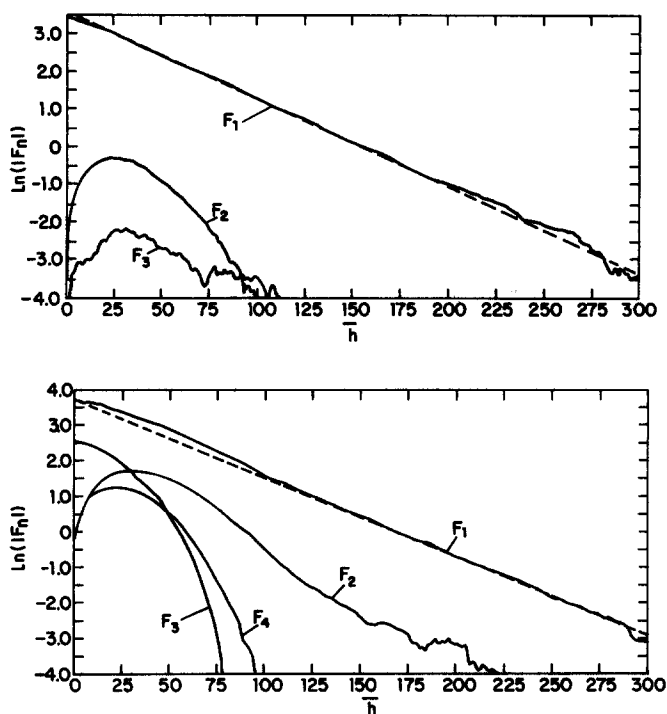


FIG. 7. Evolution of the Fourier coefficients describing the surfaces shown in Fig. 6. (a) shows the results obtained from the sinusoidal surface and (b) shows the results obtained from the square wave surface. d is the average depth of material removed (the number of sites removed is $d \times l$ where l is the strip width).

more quantitative fashion the Fourier cosine coefficients have been measured for the surface sites (the shaded sites in Fig. 1). The surface sites do not describe a single valued function of the distance x measured along the direction of the mean surface. The quantities actually measured in our work are defined by

$$F_n(\bar{h}) = \sum_{i=1}^N (h_i - \bar{h}) \cos(2\pi n x / \lambda). \quad (5)$$

In this equation $F_n(\bar{h})$ is the n th "Fourier coefficient" at the stage where the mean surface height has been reduced by \bar{h} lattice units and λ is the wavelength of the original sinusoidal or square wave pattern.

Figure 7 shows how the first few coefficients [$F_n(\bar{h})$] evolve as the surface is eaten away. It appears from this figure that the coefficient F_1 decays exponentially with \bar{h} after a short initial regime in which the deviation from exponential behavior is greater than the statistical uncertainties associated with our simulations. The asymptotic decay of the higher coefficients is probably also exponential but our statistical uncertainties are too large to investigate this. In any event, the higher coefficients seem to decay more rapidly than F_1 (after an initial period in which they may grow from an initial value of zero). In order to obtain the results shown in Figs. 7(a) and 7(b), data from a number of simulations was averaged [66 for Fig. 7(a) and 54 for 7(b)].

We have not carried out similar simulations in three dimensions however the observation that surfaces formed as a result of three-dimensional diffusion limited annihilation are even smoother than those formed in two dimensions (*vide supra*) indicated that in this case also the Fourier coef-

ficient describing the surface structure will also decay rapidly (exponentially) as the surface is eaten away.

DISCUSSION

Based on simulation results, Jullien and Botet¹⁵ have suggested that for the Eden model^{1,2,4,18} ξ may scale with the square root of l for $d = 2$, logarithmically for $d = 3$ and may saturate for $d \geq 4$. This behavior has also been observed in a variety of equilibrium models used to simulate roughening transitions.²⁷⁻²⁹ Similar behavior is found here for the diffusion limited annihilation model except that the scaling relationship between ξ and l for the diffusion limited annihilation model in dimension d is similar to that found in the Eden, roughening transition, and ballistic deposition models in dimension $d + 1$.^{27,30} In the ballistic deposition, model $\xi \sim l^{1/2}$ for $d = 2$ and ξ depends logarithmically on l or on a smaller power of l for $d = 3$.³⁰ We do not know if the diffusion limited aggregation model should behave like the ballistic deposition model in a dimension one higher. However, this may be related to the fact that random walks have a fractal dimension of 2 whereas ballistic trajectories have a fractal dimension of 1.

Since random walks eventually visit all sites in two dimensions but do not in three dimensions we had anticipated that diffusion limited annihilation might lead to rougher surfaces in three dimensions than in two. However, a much larger fluctuation in the number of particles arriving at a given region on the surface is required to create a "hole" with a characteristic size δh in a three-dimensional surface than in a two-dimensional surface.

We had, of course, expected to get relatively smooth surfaces because of the strong screening of random walkers by absorbing material. This screening effect creates very rough structures in the diffusion limited aggregation (DLA) model of Witten and Sander where the most exposed part of the surface has the highest growth probability. But in the reverse process the same affect leads to "smooth" surfaces. In the diffusion limited annihilation process, the most exposed parts of the surface have the highest probability of being removed and the most deeply buried surface sites have the smallest probability of annihilation. This strong tendency to form smooth structures is opposed only by random fluctuations in the number of walkers reaching a particular region on the surface.

In diffusion limited aggregation, the asymptotic (large size) structure is strongly influenced by lattice anisotropy.³¹⁻³³ At very large sizes,³³ the cluster has a cross-like shape with four arms directed along the axes of the square lattice. The length and width of these arms scale differently with increasing cluster mass. This suggests that the reverse process considered here might also be dependent on the orientation of the surface on the square lattice. We do not believe that the way in which the variance in the surface height (ξ) scales with the surface size (l) will be dependent on the orientation of the surface on the lattice. However, it is quite possible that the surface thickness (ξ) will be different (by a constant factor independent of l) for different surface orientations. Such behavior has been found recently for the Eden model.^{20,34}

Our two-dimensional simulations of etching through in-

ert masks indicates that grooves with sharp corners cannot be expected to occur naturally as a result of diffusion limited processes. Evidently, particles following (preferably collimated) ballistic trajectories would be more effective for this purpose.

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