**Final Report
Submitted to
DEPARTMENT OF ENERGY**

PROJECT TITLE:

DISORDER AND SELF-ORGANIZATION ON SURFACES

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GRANT NUMBER: **DE-FG02-95ER45546**

PERIOD COVERED: **9/1/98-2/28/02**

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1. Diffusion limited aggregation and fractal growth

In the grant period we completed three projects on diffusion-limited aggregation [DLA]. The DLA model [Witten and Sander, 1981] describes growth limited by diffusion in the presence of noise. It has been shown to be useful in applications in materials science, chemistry, biology, etc. (For a recent review see [Sander 2000], or the book by Meakin [Meakin 1998]). Our original paper has been cited about 2100 times in the last 21 years, and there is considerable ongoing work by many groups.

The model is very simple: we start with a nucleation center, and launch a series of random walkers, one at a time. When the first walker comes into contact with the center it attaches and becomes part of the aggregate; the next can attach to either particle of the existing aggregate, and so forth. The clusters thus grown are irregular in outline because of the Mullins-Sekerka instability [Mullins, 1963]: advancing fingers trap random walkers and screen the rest of the aggregate. This is the fundamental origin of the complexity of DLA: it is in a *fingering instability*. The proliferation of the fingers gives rise to the fractal pattern. For an example, see Figure 2. The relationship to the experimental pattern of Figure 1 is clear: adatoms on a surface are random walkers that attach to the growing island.

Another physical system that displays the fingering instability is the displacement of an inviscid fluid by a viscous one, the viscous fingering problem. It has been suspected since the work of Paterson [Paterson 1985] that the large scale features of DLA patterns are similar to those in radial viscous fingering, and I have supported this by simulation [Sander 1985]. Both problems are examples of Laplacian growth (cf. below), where the pressure (in the viscous case) or the random walker probability (in the DLA case) obey the Laplace equation. The theory of viscous fingering is quite well developed [see Meakin 1998]. A salient result is that in a channel geometry there is a single viscous finger independent of initial conditions, which can be completely analyzed. In radial geometry time-dependent patterns arise which look like DLA and analysis is difficult.

1a DLA in a wedge

In our work first DLA paper [Kessler 1998] we applied insights taken from the results of Ben-Amar

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[Ben-Amar 1991] for viscous fingering in a *wedge* which, in some sense, is intermediate between a channel and the radial.. Their result is that in a wedge of any angle the selected finger grows in a self-similar way. For fixed surface tension fingers are stable for a finite time, and it then become unstable against tip-splitting. To related this to DLA we think of each 'major finger' in the DLA cluster as growing in an *effective wedge of its neighbors*, and this effective wedge is determined self-consistently. Within the wedge, despite the many tip-splittings, the finger retains its integrity because of finger competition: if fingers split in a wedge that is too narrow, they will compete, and one will die. The result will be a finger with sidebranches. On the other hand, if the wedge is wide enough, then the fingers will not compete, and there will be two branches to the pattern. The critical wedge angle, α , at which this begins to happen will be twice the typical angle between fingers.

We verified our ideas by giving an analytic estimate for α , and then showed that it is reasonable by considering simulations of DLA clusters in a wedge. In our analytic estimates we considered two steady-state fingers side by side in a wedge with periodic boundary conditions at the sides, and estimated how large the angle must be so that there is no competition between them. One estimate is made by replacing the problem with a simpler one that we can solve analytically, that of two *needles* in the wedge. This gave an estimate of 60° for the wedge angle. A more complex estimate allowed us to give a self-consistent version of the theory taking the fractal substructure of the finger into account, and we arrived at a very good estimate of the fractal dimension of DLA. We then supported the whole picture by showing that the angular correlation function for DLA in a wedge changes character at an angle near to that of a regular pentagon.

1b Conformal maps

A very promising recent development in the study of diffusive growth problems is the method of iterated conformal maps introduced by Hastings and Levitov (HL) [Hastings, 1998]. My group has been involved in using their method in two papers [Davidovitch 1999, Somfai, 1999].

The conformal map method uses the Laplacian growth [see Sander 2000] version of DLA. In this approach we put down equations for the random walker density, u , but now use the surface of the aggregate as an absorbing wall which grows according to the arrival of flux:

$$\partial_t u = v \nabla^2 u; \quad u_s = 0; \quad v_n \sim \partial u / \partial n \quad (1)$$

Here v is the diffusion constant and v_n the growth velocity of the surface of the aggregate. For slow growth (low density of walkers) we can put $\partial_t u = 0$. Then u obeys a Laplace equation, and can be thought of as a potential; the boundary condition on the surface of the aggregate is the same as on a grounded conductor.

A very useful technique in any electrostatic problem is the method of conformal mapping. We consider the cluster to be a grounded conductor in the complex z plane, with a probability to grow at a point on its surface proportional to the charge there: $\partial u / \partial n$. The boundary conditions on the potential, u , are unit flux at infinity and $u=0$ on the surface. For radial DLA we construct a complex potential such that $\text{Re}(\psi)=u$, and define $w=\exp[\psi]=Z^{-1}(z)$. $Z(w)$ is a conformal map which takes the exterior of the unit circle in the w plane to the exterior of the DLA cluster in the z plane, and is linear for large w . The growth probability is $|dZ/dw|^{-1}$. Intervals $d\theta$ on the unit circle in the w plane correspond to intervals of arc length ds with equal growth probability in the z plane. (For more details see [Davidovitch 1999]).

HL gave an iterative method for constructing the map: suppose we know the map Z_N for N particles. Then we find a conformal map, ϕ , from the unit circle to one with a bump. Its image under Z_N is the N -particle aggregate with a bump, i.e. an extra particle. We need to adjust the size of the bump (using dZ_N/dw)

to be constant in the physical plane.* Then we compute the map with $Z_{N+1}(w) = Z_N(\phi(w))$. This is a practical procedure, though slow: it takes of order N^2 steps to grow an N particle cluster. A sample result is shown in Figure 2.

Our first paper in this area was an extensive investigation of the method which revealed many important results. The new results of this paper pertain to the scaling behavior of the Laurent coefficients of the conformal map. We write:

$$Z_N(w) = r_0 w + A_0 + \sum A_j / w^j \quad (2)$$

where r_0 is a suitably defined mean radius, and A_j are the Laurent coefficients.

The A_j turned out to have an interesting physical interpretation: they are closely related to the multipole moments of the 'charge' on the surface of the grounded cluster. We presented a theoretical discussion of the scaling with N of the A_j and pointed out the relations to the multifractal analysis of the harmonic measure, and derived scaling relations.

One result which appeared in this paper is the apparent sharpness of the distribution of the radius of the cluster. That is, it appeared from our results that the relative fluctuation of the radius, $\delta r_0 / r_0$, in an ensemble of clusters of the same N would vanish with N , so that clusters become more and more well defined. This is hard to understand for a fractal, where we expect δr_0 to scale the same as any other length. In fact, in our next paper we showed that what was really happening is a very interesting and hitherto unexpected slow crossover.

*Later we will have occasion to also change the shape of the bump.

Figure 2. A DLA cluster generated by the HL method.

Our next paper [Somfai 1999] explored the crossovers systematically. We introduced another, and much faster way to get the map which is of order $N \ln(N)$: we use the original DLA model to grow the aggregate by the very sophisticated methods now available. Then we stop at stage N and record where M random walkers would attach to the cluster. This gives a set of points z_m . These are at angle $\theta_m \sim 2\pi(m/M)$ in the w plane, since we are sampling the probability. The A_j are the Fourier coefficients of the function $z(\theta_m)$. We have used this method to find the map up to $N \sim 10^6$.

This numerical procedure allows us to find the map for very large N , and leads to many insights analytical progress. We showed analytically that the growth zone of Plischke and Racz [Plischke 1984] (the place where new growth occurs, and which seems to increase more slowly with N than r_0) must scale with the radius in the limit of large N . We used only some weak assumptions about the multifractal spectrum. The reason it *appears* to scale differently is a slow crossover (a large correction to scaling) with a very small crossover exponent, ~ -0.3 . And we showed numerically that $\delta r_0/r_0$ has the *same* crossover, which disposes of the paradox in our earlier paper. The crossovers are very interesting in their own right. They can be related to the slow approach to asymptotic behavior of the lowest multipole moments of the probability (i.e. the first few A_j).

2 Chemical reaction modeling

During the grant period we did two projects on models of chemical reactions on surfaces. [Warren 2000, Warren 2001]. The application of this work to materials science is clear: chemistry of adsorbed species is the cornerstone of materials growth and of catalysis. We been interested in reaction fronts in catalysis for some time [Goodman 1995, Sander 1996].

Our point of view is to look at such fronts from the point of view of microscopic models rather than using the more conventional technique of reaction-diffusion equations. Our goal is to see to what extent the results of reaction-diffusion theory are robust when fluctuations and correlations are included. The work we describe here (which will continue in the present proposal) concentrates on chemical reactions for which fluctuation effects are very large. In continuum terms these are called 'pulled' fronts (described by the Fisher-Kolmogorov equation); in microscopic language we call them epidemic models.

In the mathematical theory of pattern formation the Fisher-Kolmogorov equation (FK) [Fisher, 1937, Kolmogorov, 1937] plays a special role. The equation can be written:

$$\partial \rho / \partial t = \nabla^2 \rho + \rho(1-\rho) \quad (3)$$

This is a natural equation to use for infection processes such as spreading of a bacterial colony since it describes the propagation of a stable state into an *unstable* one via a moving kink. It assumes that there is no barrier to infection: once a bacteria arrives by diffusion, it reproduces unless it is limited by overcrowding (i.e. $\rho \approx 1$). It also applies to the autocatalytic chemical reaction $A+B \rightarrow A+A$ [Riordan 1995, Mai 1996]. This is an infection model because a single A in a system of B's will eventually 'infect' (convert) them all. The object of interest is the rate of spread of the infection. To see the relation to the FK equation write:

$$\partial a / \partial t = v \nabla^2 a + kab; \quad \partial b / \partial t = v \nabla^2 b - kab \quad (4)$$

Now set $a+b=\theta$ =total concentration, and note that θ is conserved for this reaction. Thus:

$$\partial a / \partial t = v \nabla^2 a + ka(\theta-a) \quad (5)$$

which becomes the FK equation after a change of variables.

The mathematical theory of the FK equation well-known [Murray 1993]. In 1 dimension kinks exist for any velocity $c \geq 2$. Restoring units, for Eq. (5) $c \geq 2(kv\theta)^{1/2}$. Velocity selection is a famous and subtle problem. Kolmogorov, et al. showed that for an initial kink which decays quickly enough (e.g. is bounded above by e^{-y}) the selected velocity is the minimum, namely 2.

There are two effects that are not considered in Eq. 3, but which a microscopic model naturally includes (as, presumably, does the real physics) namely *discreteness* of bacteria or chemical reactants and *noise*. Eq. 3 is structurally unstable against corrections of this sort. For example simulations of the model $A+B \rightarrow 2A$ show a velocity *much less than* 2 [Mai 1996].

Brunet and Derrida [Brunet 1997] altered Eq. 3 to replace $\rho(1-\rho)$ by $\rho(1-\rho)\alpha(\rho)$ where $\alpha=0$ when $\rho < \epsilon$ in order to account for discreteness. My group studied the same question [Kessler 1998] and showed, in agreement with their paper, that a microscopic model with *large concentration* (large θ in Eq.3) and *small reaction rate* (small k) is described by Brunet-Derrida theory. Discreteness of particles gives rise to a correction to the velocity which goes as $1/\ln^2(\epsilon) \sim 1/\ln^2(\theta)$, making the approach to continuum theory very slow. (Normally such corrections are of order $e^{-\theta}$).

In the work under this grant we looked back at [Mai 1996] and showed that the front propagation in their model is not controlled by discreteness at all, but rather by noise, because Mai et al. considered *small concentration* and *large reaction rate*. In [Warren 2000] we studied a version of $A+B \rightarrow 2A$ in this regime in one dimension, and we managed to solve the problem exactly. By studying our solution, we are able to see that the small velocity is a *giant fluctuation* effect which goes qualitatively as follows. The velocity is a monotonically increasing function of θ , but, for small θ there are large fluctuations in the local density. The front will move quickly through high density regions, and get stuck in the low density ones. Thus, on

average, the motion will be dominated by configurations where the front is behind a gap in the distribution of B's, that is, there is a depletion zone selected by the dynamics. We supported this picture by detailed simulations.

We returned to this problem in [Warren 2001] to see to what extent the low-dimensional result persists in higher dimensions. In 2d, though the noise effects are smaller, we also find a depletion zone, and a dependence of velocity on concentration significantly different from the mean field result. 2d may be the critical dimension of this process. We also studied the effects of noise on the wandering of the front as in our earlier work [Goodman 1995]. We found, in contrast to other, more typical systems, our pulled front has a wandering very different from the generic KPZ-like behavior [Kardar 1986].

3 Electrochemistry of Pt surfaces

The work described in this paragraph was begun during the previous grant period, and finished up in this one. There have been two major publications [Orts 1998a, 1998b]. The background is that there have been important developments in the electrochemistry of well-defined single crystal metal surfaces due to the availability of clean well-characterized samples. A classical electrochemical technique, cyclic voltammetry, provides a simple way to investigate the dynamic processes taking place at the interface. Qualitative information can be gained from it such as surface orientation, distribution of adsorption sites, and, of particular interest for this work, adsorbate islanding. The experiments were done by a group from the Universidad de Alicante (Spain) together with a collaborator from the University of Paris. I worked with this group and a theorist at Alicante on modeling one of their experiments which shows spontaneous ordering of CO adsorbed on a Pt electrode.

The Pt(111)-CO system is a model system both in surface electrochemistry and in ultrahigh vacuum surface science. The interest in the system arises both from basic science and because CO is the stable residue formed in the incomplete combustion of fuels. In the case of electrochemical systems, it is easily formed as the product of dissociative adsorption of simple oxygenated molecules such as formic acid, methanol, ethylene glycol, etc.

The feature that interested us occurs for CO adlayers adsorbed by direct dosage from CO solutions in acidic electrolytes: [Feliu 1990, Palaikis 1988]. The main experimental results are as follows: At low coverages a single peak is observed in the voltogram; as the CO coverage, θ , is increased the intensity of this peak decreases and a second peak appears at higher voltages; at high coverage only the second peak remains. These results mean that there are *two types of arrangement of CO* on the surface [Feliu, 1990] one easily oxidizable at low coverages, and a second one in which the CO molecules form compact domains which are more difficult to oxidize, at high coverages. We tried to understand the physical basis for the formation of this structure, and to model the experiment.

In our model the CO are distributed as follows: i) For $\theta < 1/3$ we assume that all CO occupy the sites in a $\sqrt{3} \times \sqrt{3}$ sublattice, and, ii) for $\theta > 1/3$ some of the CO are distributed as in i) and some form 1×1 compact islands with no defects inside. The motivation for choice i) is that we expect water to cover the whole substrate. It has been suggested [Wagner, 1993] that a good deal of insight can be gleaned for the near-surface distribution of water on Pt by considering the configuration of *ice* near Pt(111). For this structure the empty sites on the Pt surface (those most easily available for CO adsorption) form a $\sqrt{3} \times \sqrt{3}$ sublattice. Above $\theta = 1/3$, water will be displaced, and the order of the displacement is governed by the relative strengths of the various interaction terms. Both CO-CO and water-CO interactions are known to be repulsive. We assume the latter to be stronger than the former. This, together with the strong attractive interaction between water molecules justifies the formation of compact islands and allows us to explain the experimental voltograms in a satisfactory manner. The good agreement with experiment with only a few adjustable parameters gives us confidence that we have a good picture of the basic electrochemistry of this

system.

Students

During the grant period one student, E. Somfai, got his degree. Another student, C. Warren is a candidate for a degree, and should finish in this year.

Papers and preprints produced

1. J. M. Orts, E. Louis, L. M. Sander and J. Clavilier, "*Numerical Simulation of the voltammetric electrooxidation of CO adsorbed on Pt(111)*" *Electrochimica Acta* **44**, 1221-1227 (1998).
2. D. A. Kessler, Z. Olami, J. Oz, I. Procaccia, E. Somfai and L. M. Sander, "*Diffusion-limited aggregation and viscous fingering in a wedge: evidence for a critical angle*" *Phys. Rev. B* **57**, 6913 (1998).
3. J. M. Orts, E. Louis, L. M. Sander, J. M. Feliu, A. Aldaz and J. Clavilier, "*Monte Carlo simulation of CO adlayers electrooxidation on Pt(111)*" *Surf. Sci.* **416**, 371 (1998).
4. E. Somfai and L. M. Sander, "*Strain in heteroepitaxial growth*" (preprint cond/mat 9909328).
5. B. Davidovitch, H. G. E. Hentschel, Z. Olami, I. Procaccia, L. M. Sander and E. Somfai, "*Diffusion limited aggregation and iterated conformal maps*" *Phys. Rev. E* **59**, 1368 (1999).
6. E. Somfai, L. M. Sander and R. C. Ball, "*Scaling and crossovers in Diffusion Limited Aggregation*" *Phys. Rev. Lett.* **83**, 5523 (1999).
7. C. Warren, E. Somfai. and L. M. Sander, "*Velocity of front propagation in 1-dimensional autocatalytic reactions*" *Brazilian Journal of Physics* **30**, 157-162 (2000).
8. L. M. Sander, "*Diffusion limited aggregation, a kinetic critical phenomenon?*" *Contemporary Physics* **41**, 203-218 (2000).
9. C. P. Warren, G. Mikus, E. Somfai and L. M. Sander, "*Fluctuation Effects in an Epidemic Model*" *Phys. Rev. E* **63**, (2001).

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