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Growth and Percolation of Thin Films: A Model Incorporating Deposition, Diffusion and Aggregation

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Abstract – We propose a model for describing diffusion-controlled aggregation of particles that are continually deposited on a surface. The model, which incorporates deposition, diffusion and aggregation, is motivated by recent thin film deposition experiments. We find, that the diffusion and aggregation of randomly deposited particles "builds" a wide variety of fractal structures, all characterized by a common length scale L_1. This length L_1 scales as the ratio of the diffusion constant over the particle flux to the power 1/4. We compare our results with several recent experiments on two-dimensional nanostructures formed by diffusion-controlled aggregation on surfaces.

Understanding the processes underlying the growth of thin films has led to widespread interest, both from the physical and technological points of view. *Equilibrium* ("thermodynamic") models have been developed and applied with some success to the film-substrate system. However, recent dramatic improvements in experimental techniques—such as scanning tunneling microscopy—permit investigation of atomic details of the embryonic "sub-monolayer" stages of nanostructure film growth, and recent experimental work has recognized the importance of *out of equilibrium* (kinetic) effects on the determination of the observed morphologies.

Addressing such out-of-equilibrium effects is important if one is to be able to control the morphology of submonolayer nanostructures. There exists some recent research on out-of-equilibrium models—for example, models such as percolation have been developed to describe surface deposition. However percolation assumes that the deposited particles do not diffuse after being deposited, when in fact not only diffusion but also aggregation of the diffusing particles takes place. There also exist models of diffusing particles that aggregate, but such "cluster-cluster aggregation" (CCA) models do not incorporate the possibility of continual injection of new particles via deposition. Other models have been proposed, but *cluster* diffusion has never been included, nor has the percolation threshold been studied.

The model we introduce is defined as follows:

a *Deposition.* Particles are deposited at randomly-chosen positions of the surface at a flux F per lattice site per unit time.
b *Diffusion.* A cluster of connected particles is chosen at random and moved North, East, South or West by one lattice constant per unit time with a probability proportional to its mobility, which is given by $D_s = D_1 s^{-\gamma}$, where s is the number of particles in the cluster, D_1 is the diffusion constant of the monomers and γ characterizes how the mobility of a cluster depends on its size.

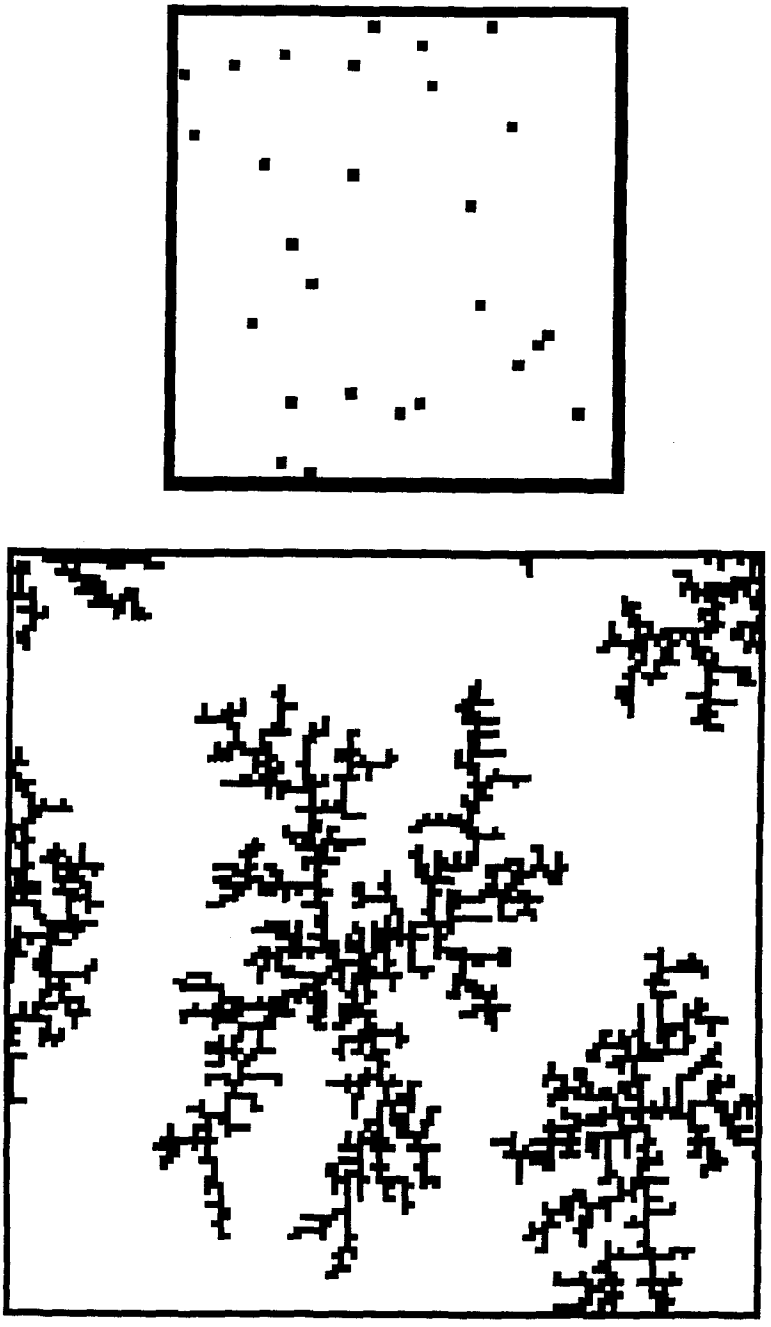

Fig. 1. Morphologies obtained in the present model for two different values of flux F, diffusion constant D_1, and total surface coverage all chosen to correspond to the experimental parameters used in obtaining the data shown in Figs. 1a and 1d of Ref.1. (a) $F/D_1 = 10^3$, and total coverage of 0.012 (b) $F/D_1 = 10^{-10}$, and total coverage of 0.12. The simulation lattice had 200 × 200 sites; the portion shown here corresponds to Figs. 1a and 1d of Ref.1, which are also a portion of the total experimental system. We set $\gamma = 10$ (large clusters rarely move—J.P. Bucher, private communication).

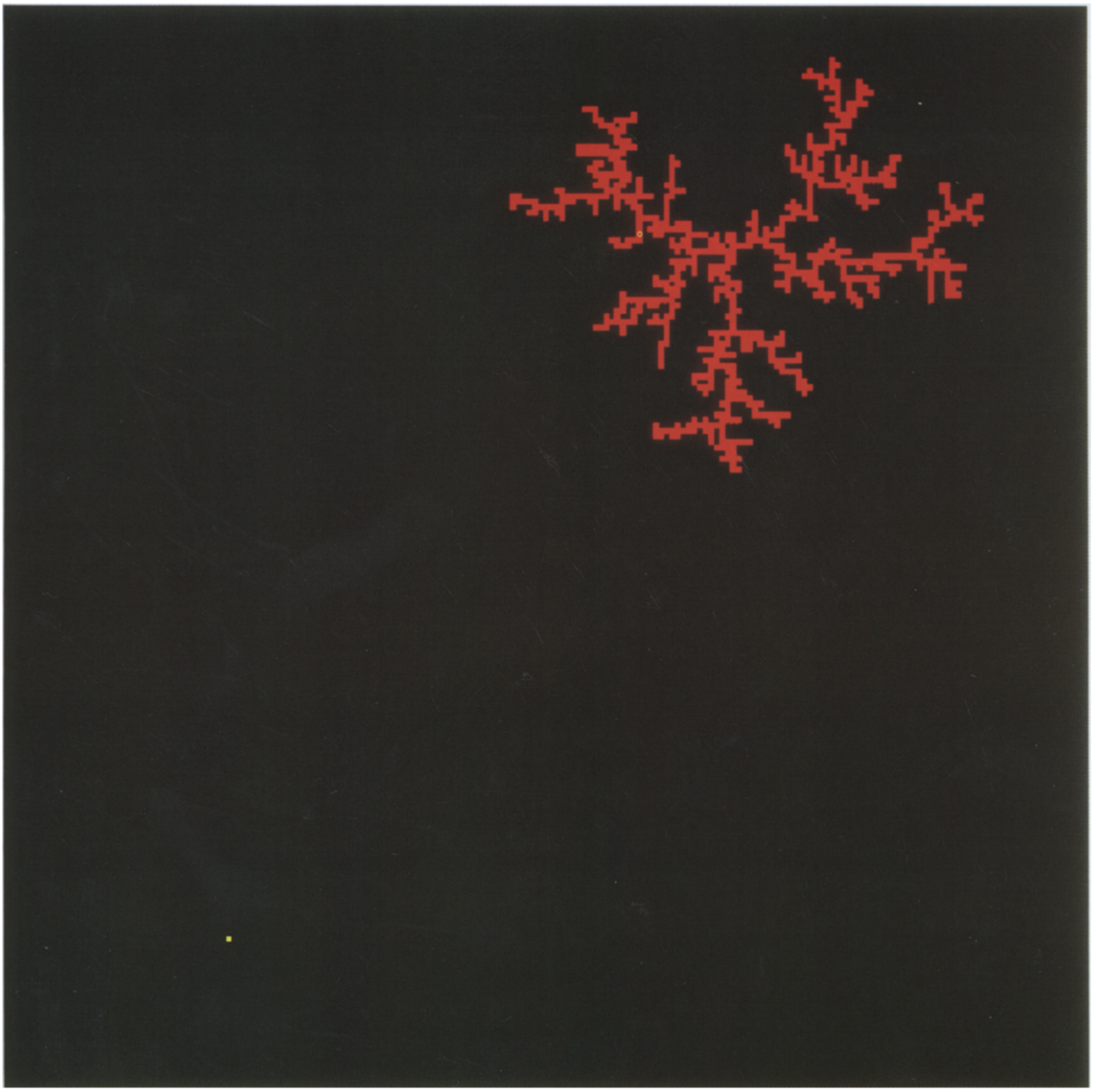

Fig. 3. *Regime I ($L < L_1$): "Particle Diffusion Regime"*. In this regime, only one cluster is present in the system. This fact is seen in (a) and (b). Since the characteristic diffusion length of a single particle L_1 is larger than the system size L, every deposited particle attaches to the already existing cluster before the next particle is deposited. At short times, the cluster is small, and virtually all the particles are deposited outside the cluster and reach it by Brownian diffusion, so we expect that the cluster should have features in common with DLA. Indeed, at short times, we find that the cluster resembles DLA (a). Its fractal dimension, measured by the sandbox method is found to be 1.7, in agreement with the expected value for a DLA cluster. At longer times, when the size of the cluster becomes comparable to the system size, a larger fraction of particles are deposited *inside* the cluster. Therefore, the model cannot be precisely the same as DLA; e.g., at the time of spanning, almost all new particles are deposited inside the boundaries of the cluster [cf. (b)].

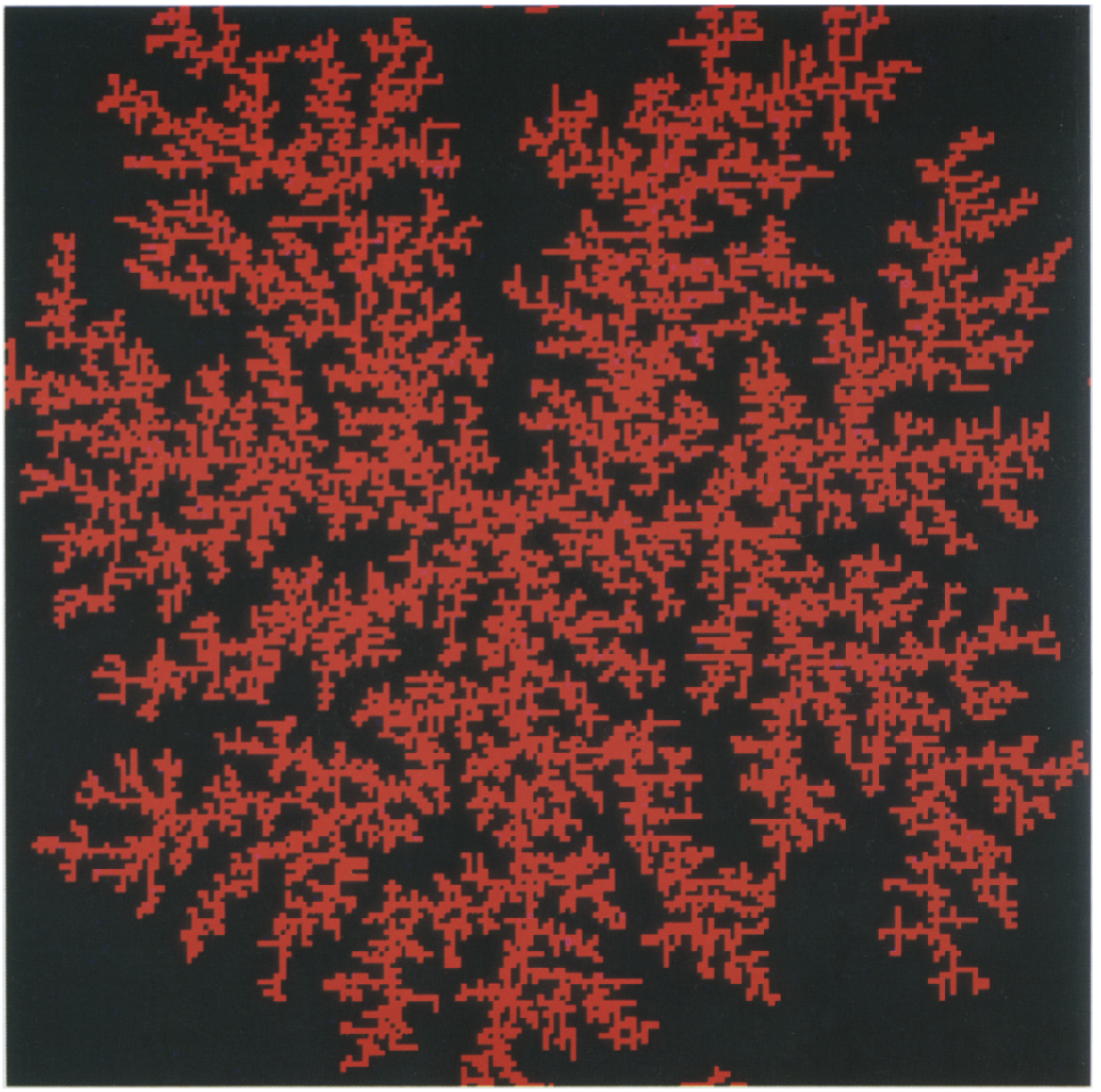

Fig. 3 (b)

Fig. 4. *Regime II ($L_1 < L < L_2$): "Cluster Diffusion Regime"*. Now several clusters are present in the system, as can be seen in (a) and (b). The reason for this is that the diffusion length is now smaller than the system size, so that several clusters nucleate on the surface. These clusters are separated by the distance set by the diffusion length L_1. We find that the spanning cluster is mainly built by the accretion of the diffusing nucleating clusters (b).

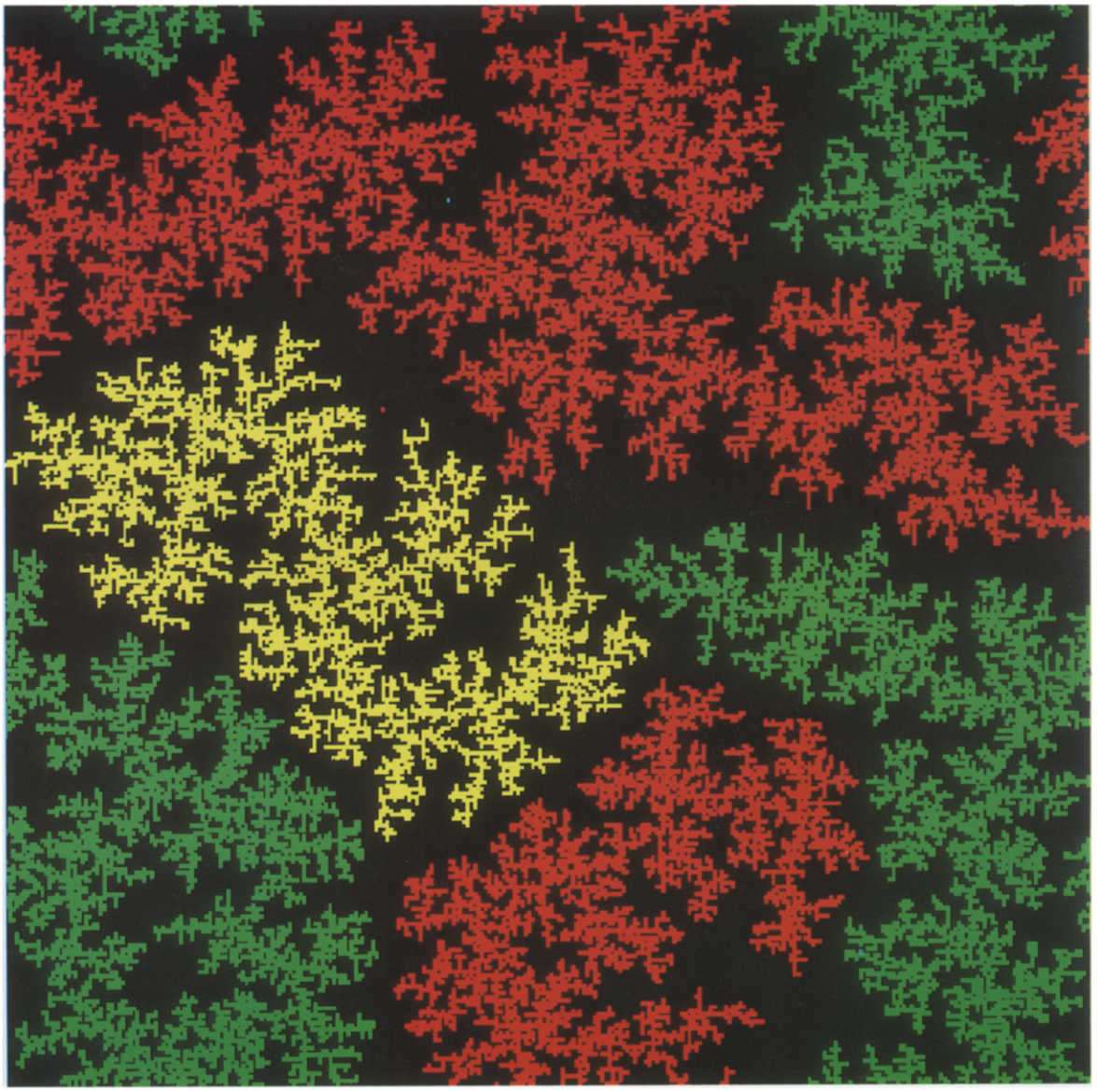

Fig. 4 (b).

Fig. 5. *Regime III ($L > L_2$): "Percolation Regime"*. At short times, many clusters are present in the system (a), and they are separated, as in regime II, by a distance L_1. At the spanning time, the system resembles a percolation network (b). The fractal dimension of the clusters as measured by the sandbox method is close to 1.9, corresponding to the value of percolation clusters. Moreover, in this regime only, we find that the total coverage scales with the system size as: $p_c(L) - p_c(\infty) \sim L^{-1/\nu}$, with $\nu \simeq 1.3$, which is in good agreement with the exponent 4/3 predicted by percolation.

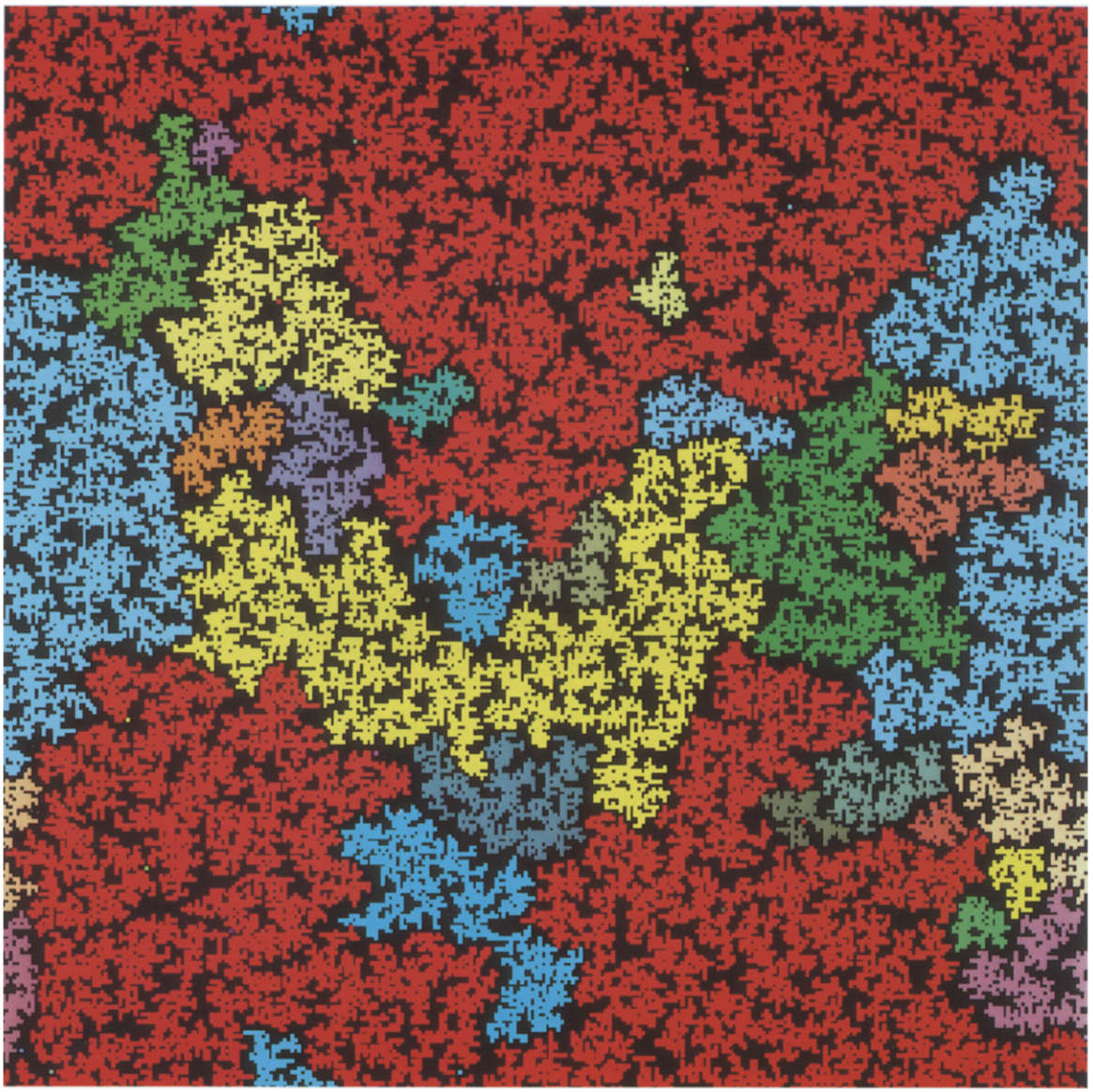

Fig. 5 (b).

c *Aggregation.* If two particles come to occupy neighboring sites, they stick irreversibly.

The model can be tested by explicit comparison with the experimental data of [1], since there are no free parameters provided we introduce the experimental values for the flux and the diffusion constant. The diffusion constant of the monomers is given by $D_1(T) = D_0 \exp(-E_d/kT)$ with $E_d = 0.14eV$ [1], and $D_0 = 5 \times 10^{11}$ [2]. Using the experimental values of the fluxes, we find $F/D_1 = 10^3$ corresponds to Fig. 1a of [1], and $F/D_1 = 10^{-10}$ to Fig. 1d. Figs.1a,b show results of the model with these flux values, and we note that the morphologies compare well with Figs. 1a and 1d of [1].

In general, the model allows one to distinguish the effects of deposition, diffusion and aggregation. We find that tuning the relative strength of, e.g., deposition and diffusion, generates a rich range of morphologies—including diffusion limited aggregation, cluster-cluster aggregation, and percolation [3]. The length and time scales characterizing these morphologies depend on experimentally-controllable parameters like deposition flux, and diffusion constant, raising the possibility that the model can be used for a controlled design of nonostructure morphologies. Indeed, the model makes specific predictions, for example that the typical size of the DLA-like structures scales as $L_1 \sim (F/D_1)^{-1/4}$.

For a fixed flux, the morphology of the system changes as a function of the system size. Figure 2 show the dependence of the "total coverage" and the "spanning cluster coverage" as functions of the system size *at the spanning time*; the total coverage is defined as the total number of occupied sites divided by L^2 and the spanning cluster coverage as the number of sites of the spanning cluster divided by L^2. We find three characteristic regimes (Figs. 3–5) delimited by two crossover length scales L_1 and L_2: L_1 is the characteristic diffusion length of a single particle on the surface, while L_2 emerges from the competition between deposition and *cluster* diffusion.

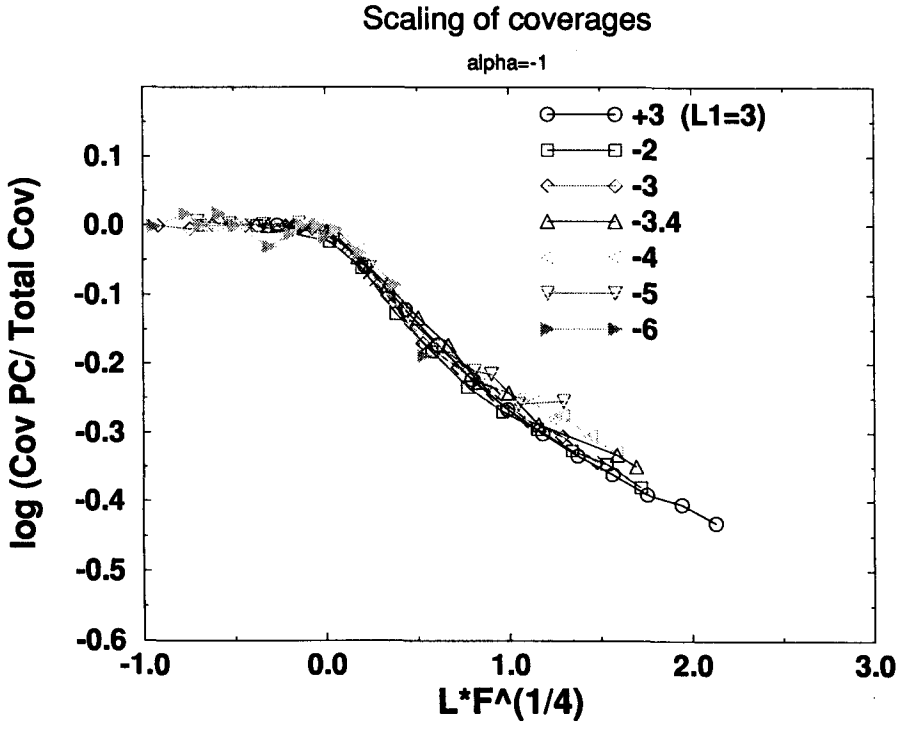

Fig. 2. Evolution of the total and spanning cluster coverages at the spanning time as a function of the system size; here $\gamma = 1$. We find three regimes of behavior (I, II and III), delimited by two length scales L_1 and L_2. For this figure, the flux is $\Phi = 10^{-4}$.

The model was originally motivated by thin film deposition experiments in which not *isolated atoms* but rather *aggregates* made up of compact spherical "molecules" $\approx$ 5 nm diameter, containing $\approx$ 2000 atoms are deposited on a surface [4]. The morphologies of Figs. 1 and 3–5 also resemble experimental images obtained by such LECBD experiments on substrates maintained at low temperatures.

In summary, we have proposed a model for describing diffusion-controlled aggregation of particles that are continually deposited on a surface. We find that the model permits one to distinguish the effects of deposition, diffusion and aggregation, and that tuning the relative strength of, e.g., deposition and diffusion, generates a rich range of morphologies—including diffusion limited aggregation, CCA, and percolation. The length and time scales characterizing these morphologies depend on experimentally-controllable parameters such as deposition flux and diffusion constant, raising the possibility that the model may prove useful in future studies seeking controlled design of nanostructure morphologies. We hope that the model may be useful in many situations where diffusion and aggregation occur in the presence of continuous deposition.

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