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Connectivity of diffusing particles continually deposited on a surface: relation to LECBD experiments

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Abstract

We generalize the conventional model of two-dimensional site percolation by including both (1) continuous deposition of particles on a two-dimensional substrate, and (2) diffusion of these particles in two-dimensions. This new model is motivated by recent thin film deposition experiments using the low-energy cluster beam deposition (LECBD) technique. Depending on various parameters such as deposition flux, diffusion constant, and system size, we find a rich range of fractal morphologies including diffusion limited aggregation (DLA), cluster-cluster aggregation (CCA), and percolation.

1. Introduction and motivation

The simple model of random percolation has, historically, been the most common model adopted to deal with systems where connectivity plays the leading role [1,2]. The percolation model is indeed helpful in understanding the influence of connectedness on the properties of the systems. However, if one is interested also on more quantitative features, there exist numerous experimental systems that cannot be accurately described by this model. Here we generalize the percolation model by including both particle deposition and diffusion. This idea arises from experiments performed with the low-energy cluster beam deposition (LECBD) technique. LECBD is a new deposition technique that allows one to deposit on a surface, instead of atoms as in the usual deposition techniques, preformed clusters (giant "molecules", ~5 nm diameter containing ~2000 atoms).

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For more experimental details, see [3]. It has been shown [4] that the percolation model is useful for understanding some features in the first stages (thickness less than a monolayer) of the growth of thin films prepared by LECBD. However, experimental evidence [5] indicates that clusters do diffuse on the substrate. In order to take into account this phenomenon, we allow diffusion of the deposited particles and interactions between them in the percolation model. Hereafter we call "particles" the preformed clusters. This new model is expected to give some insight in the growth of films prepared by LECBD (roughly until a thickness of a monolayer has been deposited). The model may also be of general interest in other situations where diffusion occurs in the presence of continuous deposition.

2. Model

The 2D percolation model can be interpreted as a progressive filling of a 2D lattice by randomly "depositing" particles (i.e., occupying sites) on it. In the classic percolation model, once a particle has been deposited in a particular site of the lattice, it will remain at this place forever. Here we propose a generalized model in which particles or clusters (i.e. the sets of connected particles, not to be confused with the 2000-atom clusters being deposited experimentally) diffuse during deposition of the other particles. We introduce a parameter F, the flux, that is the number of particles that are added to the lattice per lattice site per unit diffusion time. "Unit diffusion time" is the time needed to try to move all the clusters already present on the lattice. For example, for a flux of 10^{-4} and a lattice of $L \times L = 100 \times 100$ sites, on average, a single particle is deposited while attempting to move all the clusters (i.e. per unit time). For high fluxes ($F \gg 1$), we recover the classical static percolation model since diffusion becomes negligible. It will be seen that actually two physical processes are present in the simulations: diffusion and deposition. The system generated will be the result of the competition between these two physical ingredients, the flux F controlling their relative strength. In this paper, we focus on the growth process until the system reaches criticality, i.e., until the first connecting path occurs between the two edges of the system ("spanning time").

The simulations are carried out on a square lattice with periodic boundary conditions. The rule for diffusion is the following: clusters are picked at random and moved with a probability proportional to their mobility by one lattice spacing in one of four equally probable directions. The mobility of a cluster has been taken to be inversely proportional to its mass (its number of particles). The only interaction between particles that we study in this paper is that two particles are connected if they are nearest neighbors. They stick and diffuse together as in the cluster–cluster aggregation (CCA) model [6,7].

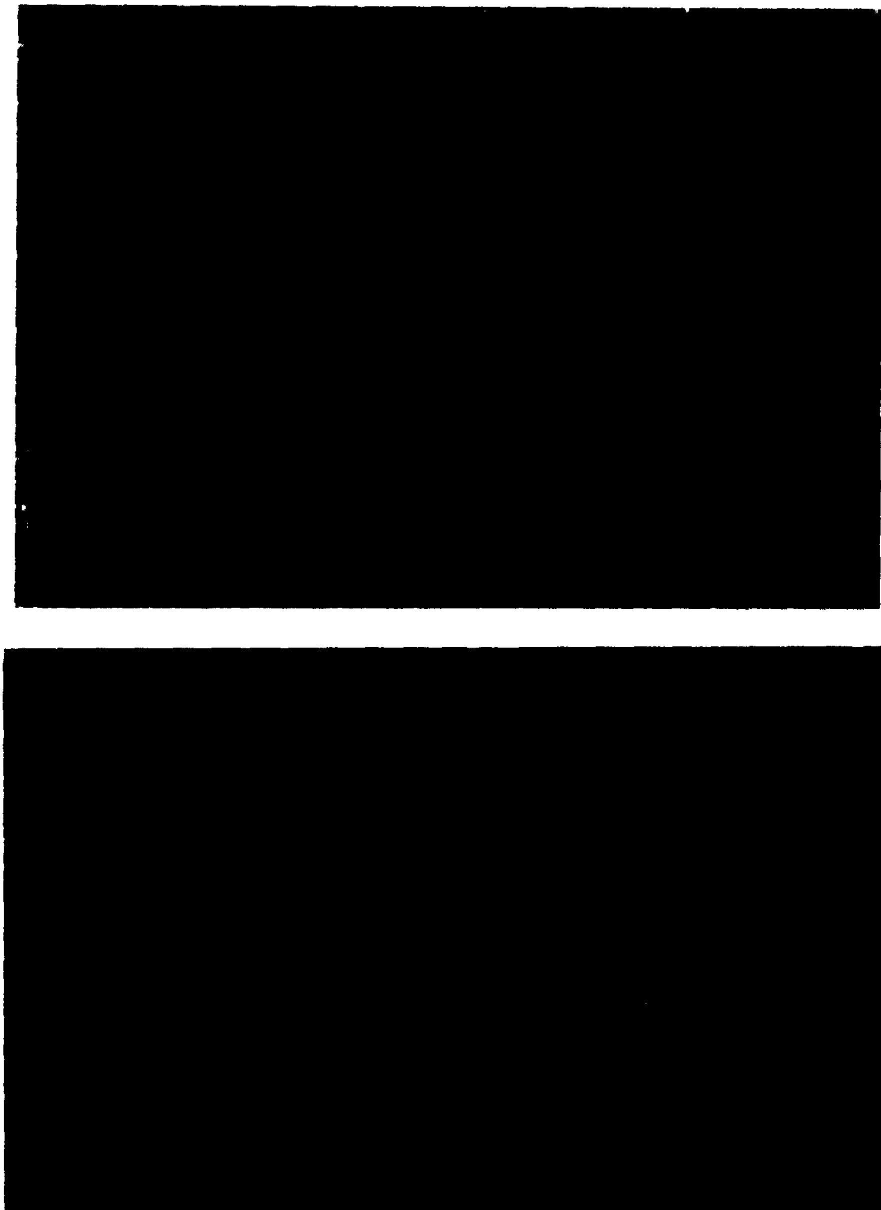
3. Results

As stated above, for very large fluxes we recover the static percolation model. The question is: what happens when diffusion becomes important? For example, in the case of classic percolation, clusters grow just by random (static) contact of two particles, leading to the well-know characteristics of percolation clusters [2]. Clearly diffusion and deposition change this picture (see Fig. 1).

For a fixed flux F, the morphology of the system changes as a function of the system size L. We find three regimes of behavior delimited by two crossover length scales L_1 and L_2, with $L_1 < L_2$. These length scales depend on the flux, both increasing when the flux decreases but we find that L_2 increases much faster than L_1. What is the physical meaning of these two length scales? We argue that L_1 is the length scale set by the diffusion of the single particles. This means that for systems smaller than L_1, the most important mechanism governing the growth of the clusters is the particle diffusion. This is so because, for that particular flux, the system size is so small that every particle added is likely to have enough time to diffuse and find the already existing cluster before another particle is added to the system. The growth of the cluster should then be very similar to the growth of a diffusion limited aggregation (DLA) cluster [7,8]. Indeed, at short times, the cluster looks very similar to DLA (Fig. 2a). Due to the deposition of particles inside the cluster, at the spanning time (Fig. 2b), the cluster is more similar to multiparticle DLA [9].

Figs. 3 and 4 show snapshots of the systems for $L_1 < L < L_2$ (Fig. 3) and for $L > L_2$ (Fig. 4). What follows is a tentative interpretation of the morphologies observed. An essential result is that now two phases of growth appear. At early times, in phase 1, "blobs" of linear size L_1 are formed. At later times, in phase 2, these blobs diffuse and connect with one another. The connection of these blobs creates large clusters of blobs ("super-blobs") and this, combined to the continuous deposition of single particles, eventually leads to the formation of a spanning cluster.

Let us study these two phases in more detail, beginning with phase 1. At short times, several clusters are formed – separated by a typical distance L_1 set by the diffusion of the single particles (Figs. 3a and 4a). The clusters grow by both aggregation of single deposited particles and diffusion of small clusters. Therefore, these clusters look similar to those obtained in the CCA model. A measurement of the fractal dimension confirms this similarity. As time increases, the clusters grow and eventually get very close to one another. At that time, the linear size of these "blobs" is roughly L_1. This is the end of phase 1. Next, two mechanisms will compete to grow a spanning cluster: (i) the diffusion of the blobs and of the "super-blobs" and (ii) the deposition of the individual particles. Even if clusters do not move, spanning will occur merely because of the filling of the lattice, just as in percolation. Diffusion of the clusters will speed the spanning.



(a)

(b)

Fig. 1. Influence of diffusion. (a) and (b) are snapshots of two systems at the *same* fraction of occupied sites or "coverage" (0.15), *same* size ($L = 400$) but with *different* fluxes. (a) $F = 10^{+4}$ (negligible diffusion), (b) $F = 10^{-4}$.

To find the physical interpretation of L_2, let us fix the flux and change the system size. For spanning to occur, super-blobs of sizes comparable to that of the system have to be grown. If the system size is very large, the super-blobs are very

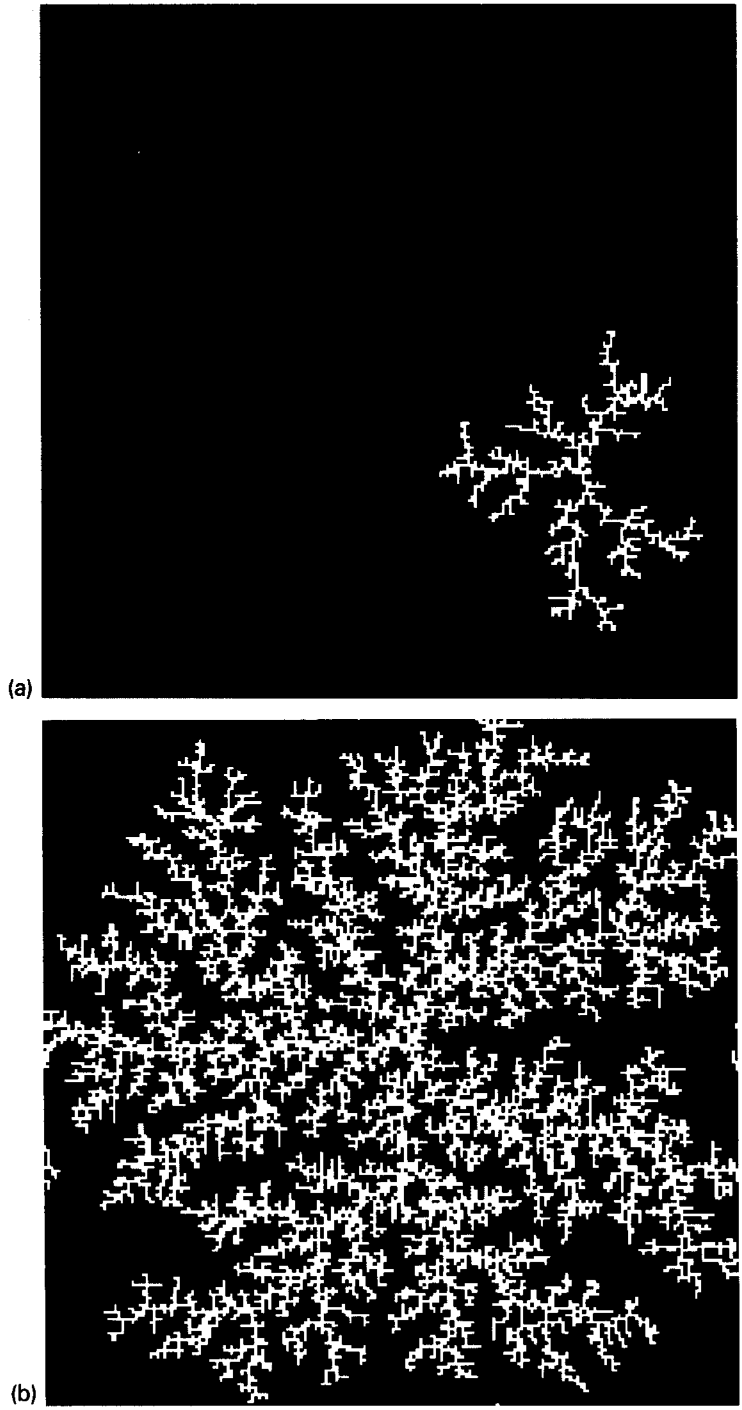
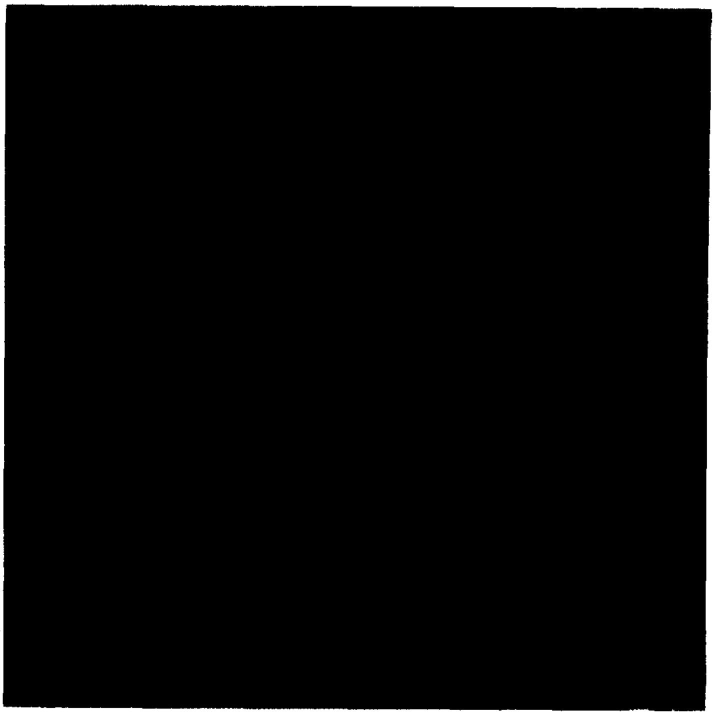


Fig. 2. System size smaller than L_1. Shown are two stages of the growth for $F = 10^{-9}$ ($L_1 \simeq 500$) and $L = 200$ sites. (a) coverage = 0.02, (b) spanning point: coverage = 0.27 (the spanning cluster is light).

(a)



(b)

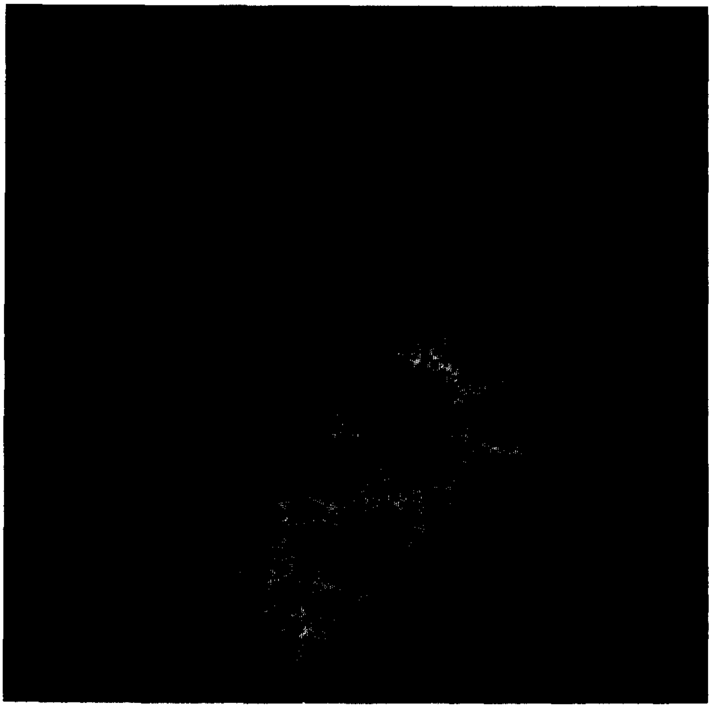
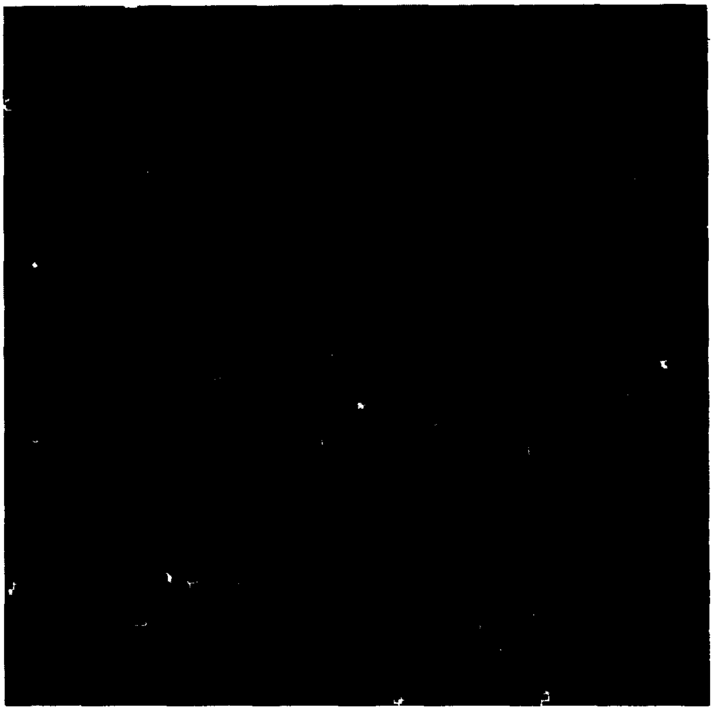
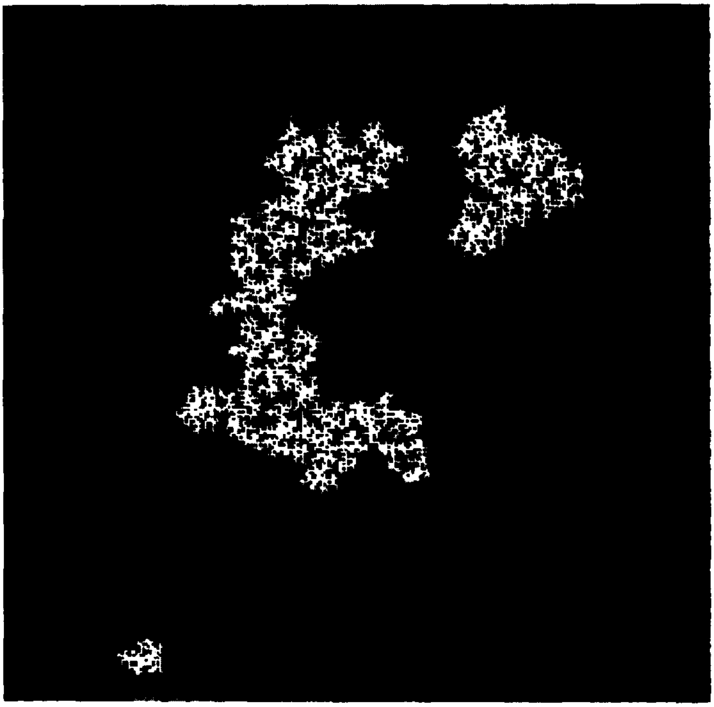


Fig. 3. System size between L_1 and L_2. Shown are two stages of the growth for $F = 10^{-6}$ ($L_1 \simeq 90$ and $L_2 \simeq 6000$) and $L = 300$. (a) coverage = 0.1, (b) spanning point: coverage = 0.31 (the spanning cluster is red).



(a)



(b)

Fig. 4. System size larger than L_2. Shown are two stages of the growth for $F = 10^{-3}$ ($L_1 \simeq 17$ and $L_2 \simeq 36$) and $L = 300$. (a) coverage = 0.1, (b) spanning point: coverage = 0.49 (the spanning cluster is red).

large (they contain many blobs of size L_1) and therefore their diffusion coefficient is extremely small. Then deposition dominates and connects the system in a percolation-like way before diffusion can do it. For smaller systems (with smaller super-blobs), diffusion is more effective and dominates the connectivity of the system. The boundary between these two system sizes is set by L_2. Indeed, the morphology of the system in Fig. 4b ($L > L_2$) looks like a percolation network. This is not the case for Fig. 3b ($L_1 < L < L_2$) because here connectivity was dominated by diffusion.

4. Summary

For $L < L_1$, the growth mechanism is very similar to DLA. The cluster grows by single addition of particles and the system spans when this cluster is large enough to "touch" the two sides of the lattice. For $L > L_1$, two growth phases appear. First "blobs" of linear size L_1 are grown. Two cases must be distinguished. For $L_1 < L < L_2$, the growth of the spanning cluster is dominated by the diffusion of the blobs. For $L > L_2$, deposition becomes dominant and the system behaves as a percolation system.

We found that the introduction of deposition and diffusion in the percolation model has interesting consequences. Depending on the flux and on the system size, different fractal morphologies are generated, as different as CCA, DLA or percolation clusters. From the experimental point of view, the structures obtained in Figs. 3a and 4a (low coverages) look very similar to some experimental images obtained by LECBD (see Fig. 3 of [5]) on substrates held at low temperatures. To account for the experimental results obtained at room temperature, in particular to understand the strong dependence of the threshold on the incident flux [10], we need to use more realistic interactions between the particles by taking into account the experimentally observed [4] coalescence of particles. This will be done in future studies.

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Note added in proof

After this work was completed, Röder et al. [11] published a series of remarkable experiments documenting the formation of nanometer-scale surface structures. Our model mimics the same process, and produces morphologies that remarkably resemble the experimental structures (e.g., Fig. 2c bears a striking similarity to Fig. 1d of [11], as sketched briefly in [12]. Also, after this work was submitted, we learned of a careful study [13] that treats a related model in which clusters do not diffuse.

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