

Microscopic model of diffusion limited aggregation and electrodeposition in the presence of leveling molecules

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We present a cellular automata approach for microscopic modeling of the effect of unbinding in diffusion limited aggregation. The automata represent active particles, which are able to change their internal state and affect their neighbors. The geometry resembles electrochemical deposition—“ions” diffuse at random from the top of a container until encountering an aggregate in contact with the bottom, to which they stick. This model exhibits dendritic (fractal) growth in the diffusion limited case. The addition of a field eliminates the fractal nature but the density remains low. The addition of molecules that unbind atoms from the aggregate transforms the deposit to a 100% dense one (in three dimensions). The molecules are remarkably adept at avoiding being trapped. This mimics the effect of so-called leveler molecules which are used in electrochemical deposition.

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I. INTRODUCTION

Roughening in electrochemical deposition is one of a class of growth problems. The two main theoretical methods of tackling the problem are continuum and microscopic methods. The continuum approach is typified by the Kardar-Parisi-Zhang equation [1] and its variants [2–4]. Microscopic methods fall broadly into two classes: Eden-type [5,6] models, which consider the deposit growing into a surrounding medium, and aggregation-type models [7], which consider diffusing particles becoming attached to the growing deposit.

This work was motivated by aqueous electrodeposition where metal cations in solution are driven by an external voltage to coat the cathode. In practical electrodeposition work, for applications from microelectronic interconnects to copper plating, the aim is usually to avoid roughening and obtain a flat surface [8,9]. Empirically, it has been known for many years that so-called levelers, typically organic molecules, can be added to control the roughness of the films [10]. The molecular-level mechanism by which these levelers work remains uncertain, several models have been proposed [10] including diffusion, chemical filming, electrosorption, complex formation, and ion pairing. A continuum model of the effect of levelers was recently advanced [11], based on the assumption that the molecules were found preferentially at high curvature regions, and have the effect of blocking further deposition there. It is likely that the dominant mechanism is system dependent.

The concentration of leveler molecules in solution is typically a few orders of magnitude lower than that of the metal ions, and the levelers are absorbed into the deposit in much lower concentration. This makes it unlikely that their effect results from strong bonding of molecules to the surface. This is borne out by *ab initio* calculations of copper and organic molecules, which show that phenyl rings are typically only weakly physisorbed to the surface of solid copper, but are strongly bound to single atoms or ions, a difference that

arises because the metal atom or ion orbitals are able to lower their energy by delocalizing and hybridizing with the phenyl states, whereas the metal surface states are already delocalized, and cannot gain much energy by further hybridization [13].

In this paper we advance a microscopic picture based on this observation. The mechanism is different from blocking—we postulate that the aromatic molecules bind to metal ions and abstract them from the growing deposit. This simple mechanism is implemented as a cellular automaton: it gives some fascinating dynamics and provides an extremely strong leveling effect.

II. THE MODEL

The model is based on the motion of autonomes [14] on a lattice in two or three dimensions. It is rule based and comprises a regular lattice occupied by three types of autonome, ions in solution (I), deposited atoms (A), and levelers in solution (L). They move on a square (cubic) lattice according to the following iterated rules.

(1) Ions and levelers are introduced stochastically at the top, with probabilities μ_I, μ_L (effectively a chemical potential), and may diffuse back out from the top.

(2) All ions move stochastically in two (three) dimensions in one of eight (26) directions, with a bias in favor of moving downward (the field E).

(3) Levelers move stochastically in one of eight (26) directions with no bias.

(4) If the randomly chosen move would take the ion or leveler onto an occupied space, no motion occurs.

(5) Ions moving adjacent to the bottom, or a continuous chain of atoms connected to the bottom, are deposited (converted to atoms, which do not move).

(6) Levelers adjacent to atoms convert the atoms into diffusing ions with “unsticking” probability p .

The model depends on four parameters, the leveler and ion chemical potentials μ_I and μ_L , the unsticking probability p , and the field E .

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The simple case without levelers is just diffusion limited aggregation (DLA) [12]. This has been well studied [15] and produces fractal geometries which can be found experimentally [16]. To make contact with previous work, it is convenient to measure the density and/or fractal dimension of the deposit rather than the surface roughness per se. The fractal nature is measured by [7]

$$\alpha = \lim_{x \rightarrow \infty} \frac{d \log[\rho(x)]}{d \log x}. \quad (1)$$

where x is the height above the bottom and $\rho(x)$ is the fraction of cluster atoms at that height. Although the boundary conditions mean that the fractal nature is manifest only in one direction, it is possible to define an effective fractal dimension for the cluster as $D = d - \alpha$ [7].

A. Two-dimensional case

First, we discuss our results for the two-dimensional (2D) case. Although not applicable to real electrodeposition, the 2D case contains most of the relevant physics.

For 2D DLA in this geometry we obtain the expected $\alpha = 0.29$ [7] (i.e., $D = 1.71$). We investigated the effect of increasing the applied field by applying a bias between downward and upward hopping of the ions—the downward hops have probability $(1+E)/8$, sideways $1/8$, and upward $(1-E)/8$. There is a finite size effect once the deposit reaches the top of the simulation cell, due to its inability to grow further. Hence the density is measured from the central 80% of the simulation, ignoring the upper and lower parts. We ran the simulation until the first “atom” reached the top, height $y = 100$, and measured the fractal dimension of the cluster. It was found that calculations on a grid 500 sites wide and 100 high with periodic boundary conditions reliably reproduced this, provided data above $y = 90$ are discarded. For size 200×100 , the region above $y = 50$ is not in equilibrium. The aspect ratio is crucial for determining finite size effects. For increased height, the fractal dimension increases toward 2 for all nonzero fields, indicating that a single deposit “tree” spans the system.

For each of our data collection runs, the fractal dimension at each field is measured from the slope of a logarithmic plot of density against height. The slope shows the fractal nature of the growth [Eq. (1)]. The onset of curvature at large heights shows regions affected by finite size effects: the upper parts of the sampling region have not reached their equilibrium density. The essentially straight lines with zero slope found for higher fields indicate nonfractal clusters, while the value of the mean density (0.3–0.5) shows that all clusters are far from compact. Five simulations were performed at various fields. From the results of each simulation we first plot $\ln \rho$ (logarithm of the density) as a function of $\ln y$ (logarithm of the height). α is the slope of this graph; the nonlinear tail to this graph for large y is excluded from the fit. The results of these with the average and standard deviation are shown in Fig. 1.

We see that when a field is added, the preferred direction breaks the scale-free fractal nature of the DLA deposit. However, as can be seen in Fig. 1 the deposit still has low density

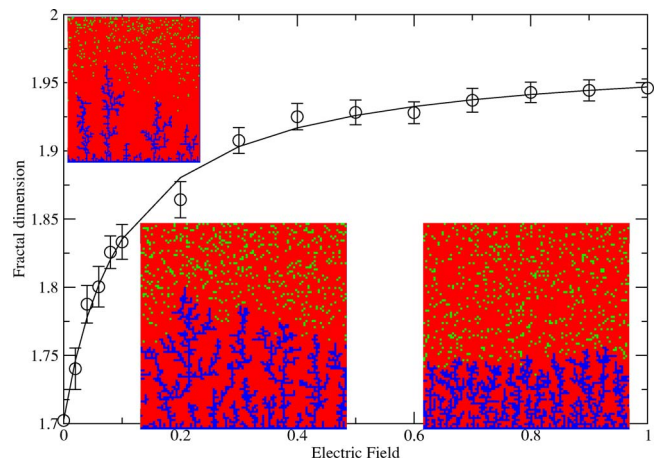


FIG. 1. (Color online) Effect of electric field on the fractal dimension of the 2D deposit without levelers. Line is a three-parameter fit $D = 1.972 - 0.27/(1 + 9.696E)$. Upper inset shows fractal growth at zero field; lower insets show snapshots of the growing deposit at $E = 0.1$ and 0.5 . The green (white) squares represent ions, the blue (dark gray) squares represent atoms, and the red (light gray) squares represent unoccupied sites (fluid).

and a rough, dendritic surface. The same is true in the 3D case. Field alone has the effect of reducing α toward zero; however, as can be seen in Fig. 1, eliminating the fractal growth does not lead to a high density deposit. It is already known that ballistic growth gives porous, nonfractal deposits; our result generalizes this result to apply to any biasing field.

The levelers have the effect of unsticking atoms from the deposit; thus the dendrite structure is cut away at its roots. This is a nonlocal process and evaluating the (dis)connected cluster is the most time-consuming computational aspect of the simulation.

The addition of even a small amount of leveler with an unsticking probability of 0.1 has a dramatic effect on the structure. The density of the deposit is increased substantially—even a $\mu_L = 0.01$ gives a dense deposit. The mechanism for this is that the levelers can diffuse into the open deposit, and undercut the fingerlike growth. Unsticking a single atom can affect quite large numbers of atoms, by undercutting structures bonded by a single connection (see Fig. 2). Once some leveler is present, increasing the unsticking probability p above a rather small threshold value (0.05 for $\mu_L = 0.01$, $\mu_L = 0.02$) does not give a significant further increase in the density. p seems to affect the densification rate rather than the final state.

The number of levelers permanently trapped by the deposit is remarkably low: by unsticking their neighbors a leveler and a vacant site can codiffuse effectively through the deposit to escape. In the model, this escape mechanism fails only at very high leveler concentration [see Fig. 4(b)], and for very high values of $p\mu_L$ the growth rate goes to zero: we discuss this zero-growth transition later.

B. Three-dimensional case

The three-dimensional case is closer to reality but harder to visualize. The principles of our calculations here are iden-

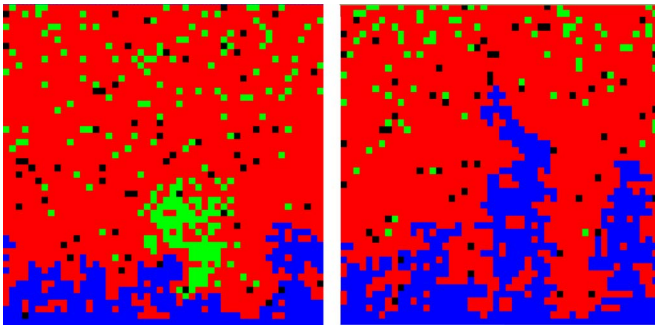


FIG. 2. (Color online) Snapshot of a leveling event. In this closeup of part of a 2D simulation, the black squares represent levelers, the blue (dark gray) atoms, and the green (white) ions. (left) The large cluster of green ions in the center of the figure have been disconnected by the action of the single black leveler at their foot, and are about to fall. (Right) Some time later, the deposit has compacted, but the large central protruberance remains.

tical to those in 2D, with the particles able to move to any of 26 adjacent sites. The results are qualitatively similar, with the introduction of a field reducing the fractal dimension without significantly increasing density. However, the effect of levelers is much more pronounced: even a small number of levelers bringing about a transition to a 100% dense phase. This might be anticipated from the existence of fluid percolation, which allows the levelers to move into the deposit, up to a much higher density. However the final 3D densities are significantly higher than the percolation threshold, very close to 100%.

In Fig. 3 we consider varying μ_L with E fixed at 0.2 for various μ_I . Density is measured as the fraction of sites occupied by an atom in the middle 80% of the grid at the time when the first atom appears in the top layer—this leads to a finite size broadening of the transition. Similar problems due to finite system size are also shown. The crossover to a dense deposit occurs for small leveler concentration, here when

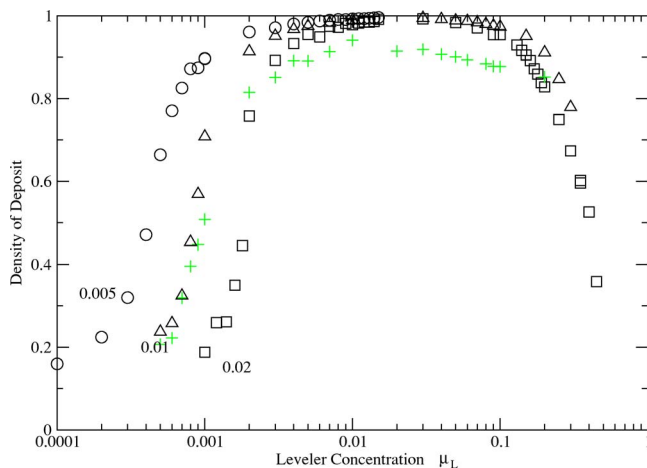


FIG. 3. (Color online) Logarithmic graph of density against concentration of leveler μ_L for 3D model, with $\mu_I=0.005$ (circles), 0.01 (triangles), 0.02 (squares), $p=1$, and $F=0.2$. Data are collected for a 100×200^2 grid. Crosses show data from a smaller 50×100^2 grid, showing a pronounced finite size effect.

$\mu_L \approx \mu_I/10$ (it also depends on the field). Reduced density is observed again at very high leveler concentration: in this unphysical regime the leveler coats the surface, and is held in place by the downward pressure of the falling ions; thus the reduced density comes from incorporated levelers, rather than an open structure. Consequently, as the leveler concentration is increased, we encounter first a crossover from dendritic to dense deposits, then another crossover to the non-growth region.

The complete compacting effect of the levelers for a sufficiently large range of concentrations is shown in Fig. 3. A concentration of leveler significantly less than the concentration of ions is required to obtain effectively 100% density (with all the levelers escaping). Varying the field under these conditions has little effect—the sample remains dense. For high $p\mu_L$, or for very low field, the deposition ceases.

Taken together the 2D and 3D results for this model of leveler action show that while field or levelers reduce the fractal dimension of the deposit, only the levelers cause a significant densification of the deposit. Moreover, even a rather low concentration of levelers with a low unsticking probability has a strong densifying effect. In 2D it is not possible to produce a fully dense deposit: the reason for this is that the large collapsing dendrites fall and enclose regions which are then inaccessible to the levelers. In 3D the lower percolation threshold leads to dense deposits.

Many cellular automata can be examined analytically in a mean field approach. The continuity equation in the relevant regime, where the diffusion is controlled by the rate of unsticking (i.e., $D=\mu_L p$), gives

$$\frac{d\rho_I(z)}{dt} = \rho_L(z)p \left(\frac{d^2\rho_I(z)}{dz^2} - EC \frac{d\rho_I(z)}{dz} \right) \quad (2)$$

where C is a geometric factor depending on the dimensionality and connectivity.

Since the levelers are unaffected by the ions, except for exclusion, $\rho_L(z) = \mu_L[1 - \rho_I(z)]$, where

$$\frac{d\rho_I(z)}{dt} = \mu_L p (1 - \rho_I) \left(\frac{d^2\rho_I(z)}{dz^2} - EC \frac{d\rho_I(z)}{dz} \right) \quad (3)$$

with the boundary conditions that $\rho_I(0)=1$, $\rho_I(\infty)=\mu_I$; the long time solution to this is $\rho_I(z)=1$. The equation permits a steady state solution given by $\rho_I(z) \propto \exp(-ECz)$; however, the boundary condition $0 < \rho_I < 1$ makes this unphysical. Thus there are two solutions consistent with the boundary conditions: either no deposition ($\rho_I=\mu_I$) or a dense deposit ($\rho_I=1$). These two limits are seen in the simulation; the first corresponds to having sufficient leveler that all deposited atoms are removed, the second to the “normal” densification case. However, the simulation finds a third regime of zero growth rate. Furthermore, the mean field approach gives a rather poor description of the dynamics.

The failure of the mean field approach neglects the fact that only discrete numbers of levelers are possible, and once levelers are excluded from a void unsticking ceases inside that void. The number of levelers incorporated permanently in the deposit is extremely small. The unsticking ability of the levelers allows them to escape, and here the value of

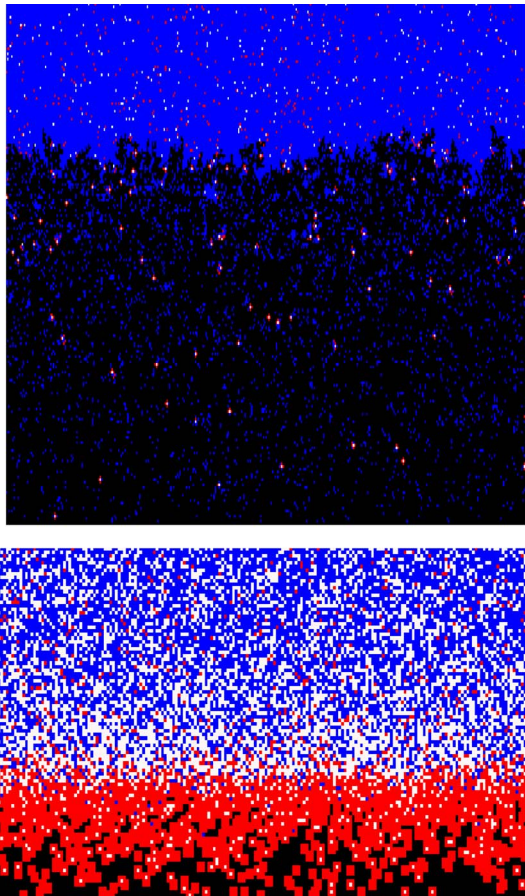


FIG. 4. (Color online) Snapshot of a slice through a growing 3D deposit. To distinguish from two dimensions, where the whole system is viewed, in three dimensions we use a blue (dark gray) background, the white represents levelers, black represents atoms, and the red (light gray) represents ions. (Left) The large cluster of (a) full system $\mu_L=0.01$, $\mu_I=0.01$, $E=0.1$ showing dense 3D deposit with leveler. (b) Detail from similar system with $\mu_L=0.2$, $\mu_I=0.01$, $E=0.1$ showing blocked zero-growth state.

unsticking probability plays a role—low unsticking probability leads to extra incorporation. Thus although the mean field model tells us that the deposit becomes 100% dense independent of dimension, one should recall that this assumption breaks down at high density.

C. Zero-growth-rate transition

In the mean field model, and in both 2D and 3D, there is a transition from a growing state to a zero-growth-rate state.

This occurs when the rate of removal of material from the deposit due to the action of the levelers is equal to the rate of arrival. Growth on a fractal surface occurs faster than on a dense one, and the effect of the levelers is that the deposit grows and densifies. The zero-growth condition then occurs for a dense deposit with a flat surface. The rate of arrival per site is then simply μ_I , while the escape rate is $p\mu_L$ times the probability that a released ion diffuses away. For a flat surface, this is approximately the probability that its first movement is upward, giving a rough estimate of the transition condition as $\mu_I/\mu_L=9(1-E)p/26$. In the simulations, we find that this type of zero growth occurs only for low fields, μ_I , and μ_L .

For high fields, μ_I and μ_L crowding occurs, with the falling ions dragging the levelers. This invalidates our mean field approximation which assumes free diffusion. This results in a dense mix of I , A , and M autonomes at the bottom of the simulation, with significant amounts of leveler incorporated in the deposit. The atom density in the deposit is therefore reduced (see Fig. 3), and the interface region contains only leveler and ions (Fig. 4) so no further growth can occur.

The ion and leveler densities in this regime are far larger than realized in experimental electrodeposition.

D. Conclusions

In summary, we have presented an extension of the diffusion limited aggregation model which describes the unbinding effect of organic molecules in microscopic detail. The model shows that a very small concentration of the leveling molecule acts to destroy the fractal structure by a catalytic-type action which enables each molecule to act multiple times. In 3D the levelers have the most striking effect, attaining deposit densities of over 99% without themselves being trapped. Only a small amount of leveler is required to densify the deposit, an intermediate amount speeds up the process, but beyond a critical level all growth ceases. Consistent with empirical practice in electrodeposition [10], the optimum amount of leveler is somewhat less than the amount of ions, depending on the underlying lattice connectivity and the unsticking probability.

The action of the leveling molecules is most easily appreciated by watching the system evolve dynamically. A java applet which enables the reader to do so in the 2D case can be seen at [17].

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