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

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Abstract

A microscopic model of the effect of unbinding in diffusion limited aggregation based on a cellular automata approach is presented. The geometry resembles electrochemical deposition - “ions” diffuse at random from the top of a container until encountering a cluster in contact with the bottom, to which they stick. The 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 which unbind atoms from the aggregate transforms the deposit to a 100% dense one (in 3D). The molecules are remarkably adept at avoiding being trapped. This mimics the effect of so-called “leveller” molecules which are used in electrochemical deposition.

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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 KPZ equation \[1\] and its variants \[2, 3, 4\]. 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 “levellers” - typically organic molecules, can be added to control the roughness of the films \[10\]. The molecular-level mechanism by which these levellers 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 levellers 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 levellers in solution is typically a few orders of magnitude lower than the metal ions, and the levellers 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 \textit{ab initio} calculation of copper and organic molecules, which show that phenyl rings are typically only weakly physisorbed to the surface of the copper, but are strongly bound to single atoms or ions. This arises because the metal atom/ion orbitals are able to lower their energy by delocalizing and hybridising with the phenyl states, however the metal surface states are already delocalized, and cannot gain much energy by further hybridisation. \[12\]

In this paper we advance a microscopic picture based on this which exhibits a levelling effect in diffusion limited growth. 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 gives some fascinating dynamics and provides an extremely strong levelling effect.

The model is based on the motion of autonomes \[13\] on a lattice in two or three dimensions.
It is rule-based and comprises a regular lattice occupied by three types of autonomous, ions in solution (I), deposited atoms (A) and molecules in solutions (M). They move on a square (cubic) lattice according to the following iterated rules.

1/ Ions and molecules are introduced stochastically at the top, with probability $\mu_I$, $\mu_M$ (effectively a chemical potential), and may diffuse back out from the top.

2/ All ions move stochastically in 2D(3D) in one of eight(26) directions, with a bias in favour of moving downward (the field, $E$).

3/ Molecules move stochastically in one of eight(26) directions.

4/ If the randomly chosen move would take the ion or molecule 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/ Molecules adjacent to atoms convert the atoms into diffusing ions with "unsticking" probability $p$.

The model depends on four parameters, the leveller and ion chemical potentials $\mu_I$ and $\mu_M$, the unsticking probability $p$ and the field $E$.

The simple case without levelling molecules is just diffusion limited aggregation DLA. This has been well studied and produces fractal geometries which can be found experimentally. To make contact with this 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

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

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 $D = d - \alpha$.

When a field is added, the preferred direction breaks the scale free fractal nature of the DLA deposit (see fig. However, as can be seen in Figure the deposit still has low density
and a rough, dendritic surface. The same is true in the 3D case. The profile of a typical simulation and its associated height-density relation is shown in Figure 2.

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

First, we consider the effect of levellers in the two dimensional 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 $\alpha = 0.29$ (i.e. $D=1.71$), levellers cause densification by undercutting the fractal dendrites of the deposit. Fig. 3

Increasing the applied field has the effect of reducing $\alpha$ to a limiting value of about 0.05. However, as can be seen in figure 4 eliminating the fractal growth does not lead to a high density deposit.

The addition of even a small amount of leveller with an unsticking probability of 0.1 has a dramatic effect on the structure. The fractal nature is lost, and the density of the deposit is increased substantially - even a $\mu_M = 0.01$ gives a dense deposit. The mechanism for this is that the levellers 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 figure 3).

Once leveller is present, increasing the unsticking probability above a rather small threshold value (0.05 for a $\mu_M = 0.01$, $\mu_I = 0.02$) does not give a significant further increase in the density. For high values of $p\mu_M$ the growth rate goes to zero: we discuss this zero-growth transition later.

The three-dimensional case is closer to reality but harder to visualize. The principles of our calculations here are identical 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 levellers is much more pronounced: even a small number of molecules bringing about a transition to a 100% dense phase. This might be anticipated from the existence of fluid percolation, which allows the molecules 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%.

The complete compacting effect of the levellers for a typical example is shown in figure
FIG. 1: Figure shows the effect of electric field on the fractal dimension of the 2D deposit without levellers. The field is applied as a bias between downward and upward hopping of the ions - the downwards hops have probability \((1+E)/8\), sideways \(1/8\) and upwards \((1-E)/8\). Once the deposit reaches the top of the simulation cell, its growth is again affected by 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, and measured the fractal dimension of the cluster and found that calculations on a grid 500 sites wide and 100 high with periodic boundary conditions reliably reproduced this provided data above \(x=90\) is discarded. Indeed we were unable to determine a finite width effect on \(\alpha\) for calculations with widths down to 100. For increased height, the fractal dimension increases towards 2 for all non-zero fields. Each datapoint was averaged over five runs to obtain standard error bars. In each run we first plot \(\ln \rho\) (log density) as a function of \(\ln x\) (log height), \(\alpha\) is the slope of this graph: in practice, the termination of the simulation when growing cluster reaches the top anywhere, causes a nonlinear tail to this graph for large \(x\), which is excluded from the fit. Line is a three-parameter fit \(D = 1.972 - 0.27/(1 + 9.696E))\). Upper insert shows fractal growth at zero field, lower inserts show snapshots of the growing deposit at \(E=0.1\) and \(E=0.5\).
FIG. 2: Plot of log density against height for 2D with various applied fields ($\mu_M = 0, \mu_I = 0.05, E$ increment from 0-0.3 in steps of 0.02). Simulation size was 200x100, - the simulation was stopped once any part the growing deposit reached $y=100$, at which point the region above about $y=50$ is not in equilibrium. Symbols (alternating circles, squares, triangles) represent actual densities averaged over five samples); lines are quadratic fits to the data. The slope in the zero field case (lowest line) shows the fractal nature of the growth, the pronounced curvature for fields of 0.02 and 0.04 shows these are 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 for higher fields indicate non-fractal clusters, while the value of the mean density (0.3-0.5) shows the clusters are far from compact. 3D behaviour is qualitatively similar, with fractal behaviour observed only for $E=0$.

A concentration of leveller significantly less than the concentration of ions is required to obtain effectively 100% density (with all the leveller molecules escaping). Varying the field under these conditions has little effect - the sample remains dense. For high $p\mu_M$, or for
FIG. 3: Snapshot of a levelling event. In this close-up of part of a 2D simulation, the black squares represent molecules, the blue atoms and the green ions. (left) The large cluster of green ions in the center of the figure have been disconnected by the action of the single black molecule at their foot, and are about to fall. (right) some time later, the deposit has compacted, but the large central protruberance remains.

very low field, the deposition ceases.

Taken together the 2D and 3D results for this model of leveller action show that while field or leveller molecules reduce the fractal dimension of the deposit, only the levellers cause a significant densification of the deposit. Moreover, even a rather low concentration of molecules with a low unsticking probability already 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 leveller molecule. In 3D the lower percolation threshold leads to dense deposits.

The problem 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. \( D = \mu M p \)), gives

\[
\frac{d\rho_I(z)}{dt} = \rho_M(z)p \left( \frac{d^2\rho_I(z)}{dz^2} - EC \frac{d\rho_I(z)}{dz} \right)
\]  

where \( C \) is a geometric factor depending on the dimensionality and connectivity.
FIG. 4: Logarithmic graph of density against concentration of leveller for 3D model, with $\mu_I = 0.005$(circles), 0.02(squares), $p = 1$ and $F = 0.2$. 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. Data is collected for a 100x200 grid. The crossover to a dense deposit occurs for small leveller concentration, here when $\mu_M \approx \mu_I/10$, (it also depends on the field). Reduced density is observed again at very high leveller concentration: in this unphysical regime the leveller coats the surface, and is held in place by the downwards pressure of the falling ions, thus the reduced density comes from incorporated molecules, rather than an open structure.

Since the molecules are unaffected by the ions, except for exclusion, $\rho_M(z) = \mu_M(1 - \rho_I(Z))$, whence

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

(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 a linear height/density profile $\frac{d\rho_I(z)}{dz} = -EC$, however the boundary condition $\rho_I < 1$, makes this unphysical. Thus there are two solutions consistent with the boundary conditions: either no deposition ($\rho_I = \mu_I$) or a dense deposit ($\rho_I = 1$).

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

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 levellers is equal to the rate of arrival. Growth on a fractal surface occurs faster than on a dense one, and the effect of the levellers 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 $\mu_I$, while the escape rate is $p\mu_M$ times the probability that a released ion diffuses away. For a flat surface, this is approximately the probability that its first movement is upwards, giving a rough estimate of the transition condition as $\mu_I/\mu_M = 9(1 - E)p/26$. In the simulations, we find that this type of zero-growth occurs only for low fields, $\mu_I$ and $\mu_M$.

For high fields, $\mu_I$ and $\mu_M$ crowding occurs, with the falling ions dragging the levellers. 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 leveller incorporated in the deposit. The atom density in the deposit is therefore reduced (see fig. 4). The ion and leveller densities in this regime are far larger than realized in experimental electrodeposition.

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 levelling molecule acts to destroy the fractal
structure by a catalytic-type action which enables each molecule to act multiple times. In 3D the levellers have the most striking effect, attaining deposit densities of over 99% without themselves being trapped. Only a small amount of leveller 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 leveller is somewhat less than the amount of ions, depending on the underlying lattice connectivity and the unsticking probability.

The action of the levelling 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 www.ph.ed.ac.uk/nania/diffusion/diffusion.html

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[14] An autonome is intermediate between a cellular automaton and an interacting agent. Typically it has both deterministic and stochastic behaviour, which are influenced by the environment. Here, for example, the molecules can diffuse stochastically, but not into occupies sites, they can react with the deposit to release Cu ions, and they can be created or destroyed at the top of the sample. See e.g. www.ph.ed.ac.uk/nania
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