Pattern Formation in Screened Electrostatic Fields

E. Louis

Departamento de Física Aplicada, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

F. Guinea and O. Pla

Instituto de Ciencia de Materiales, Consejo Superior de Investigaciones Científicas, Facultad de Ciencias C-XII, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

L. M. Sander

Department of Physics, University of Michigan, Ann Arbor, Michigan 48109

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It is shown that screening greatly diversifies the type of patterns that can grow in an electrostatic field. Screening introduces a new length scale and a nontrivial dependence on the boundary conditions. Growing patterns can either have a fractal character (diffusion-limited-aggregation–like) at scales shorter than the screening length, be similar to the Eden model, or even be dense. A transition from dense to multibranched growth occurs at a point which depends on the potentials at the boundaries, the distance between them, and the screening length.

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The diffusion-limited-aggregation (DLA) [1] and dielectric-breakdown (DB) [2] models have been very successful in illustrating the possibility of fractal growth [3] in Laplacian fields. Nature does offer, however, a much richer scenario in which both fractal and nonfractal patterns may grow. The dependence on the boundary conditions in DB discussed in Ref. [4] illustrates this point: A change in the shape of electrodes induces drastic changes in the growing patterns which evolve into a rather dense multibranched structure with fractal dimension $D \sim 2$. Although several reasons have been suggested [4] to explain such a variety of patterns, among which we mention the existence of a threshold field and the internal resistance of the breakdown pattern (plasma channels in the case of a discharge in a gas), in very few instances have their effects been analyzed in any depth. Only the possibility of a different growth law in which the growth rate is assumed to be proportional to a power, different in general from unity, has been examined in detail in the DB context and, by utilizing an equivalent approach, in DLA [5]; it has also been used to explain the more-diluted-than-DLA patterns that may occur in nature. Note, however, that there are microscopic reasons for expecting $\eta = 1$ in DB [6]. More recently, the possibility of a crossover from a DLA pattern to a more dilute one has also been investigated by using more complicated growth laws, both in DB [7] and in the somewhat similar phenomenon of mechanical breakdown [8,9]. The variety of structures further increases for the growth of metallic aggregates through electrochemical deposition (ECD). These may have a fractal character like in DLA, be dendritic crystals, or give rise to dense radial structures [10–12]; the stability of the latter has been ascribed to the finite resistivity of the aggregate [10], or to anion migration between the electrodes [12–14]. Besides, a transition from a dense pattern to a more diluted branched structure has been observed [11,14,15] and referred to as the Hecker transition [15]. To explain this sharply defined transition several mechanisms have been proposed [11,14], all having in common the interplay between the Laplace field and the diffusion field.

In this Letter we investigate the effects of screening on structures growing in electrostatic fields. The origin of screening might lie in the presence of free charges such as in the case of ECD and DB. From elementary considerations of thermal equilibrium, the Debye-Hückel theory deduces the existence of a screening length which depends on the total density of charges and the temperature [16]. The same situation may arise in DLA; in this case screening might be due to the presence of sinks (screening) or an ambient of particles (antiscreening). We have carried out numerical simulations and an analytical study along the lines proposed by Mullins and Sekerka [17]. The results show that screening leads to a much richer variety of patterns. It introduces a new length scale and a nontrivial dependence on the boundary conditions which, as discussed below, is responsible for a transition that resembles the Hecker transition. Patterns may have a fractal character at scales shorter than the screening length, be Eden-like, or grow dense. The mentioned transition (from dense to multibranched growth) is shown to occur at a point that depends on the potentials at the two boundaries, the distance between them, and the screening length.

We concentrate on the DB model [2]. In that model, a breakdown pattern is allowed to grow in a dielectric medium placed between two electrodes at different potentials. The aggregate is assumed to be a perfect conductor, and, thus, at constant potential, whereas fields in the dielectric follow the Laplace equation. To account for screening we replace the Laplace equation by

$$\nabla^2\phi = \lambda^2\phi . \tag{1}$$

Antiscreening would correspond to a minus sign on the right-hand side (RHS) of Eq. (1); its effects will be briefly discussed at the end of this Letter. To illustrate the ideas we shall restrict our investigation, as stated above, to a planar geometry (growth in a channel). Some comments on growth in a circular geometry (two dimensions) will also be made.

Numerical simulations were carried out on samples of the square lattice of sizes 100×200. The boundaries along the longest direction were taken as electrodes at constant potentials ϕ^i (inner) and ϕ^o (outer), whereas periodic boundary conditions were used in the shorter direction. To originate an aggregate the standard growth procedure [2] was followed assuming a growth rate proportional to the absolute value of the field at the surface of the aggregate. As usual Eq. (1) was solved iteratively. It has to be remarked that screening can strongly decrease the potential at the surface, changing quickly (see Fig. 1) as the pattern evolves, and thus the error used to stop the iteration process should be decreased or increased conveniently. Our criterion was that the maximum error at each node was less than 1% of the average value of the electric field at the boundary of the pattern. This gave around 50 iterations to relax the electrostatic field.

In an experiment, the external circuit fixes the potential drop, $\phi^i-\phi^o$. The average position of the potentials, $(\phi^i_{\rm rm}+\phi^o_{\rm rm})/2$, is determined by the requirement of charge conservation at all times (within the Debye-Hückel theory, the charge distribution is linearly proportional to the electrostatic potential). In our simulations, we have found that the latter constraint is well satisfied with no adjustment of the average potential once the initial values of ϕ^o and ϕ^i are given. Thus, within reasonable accuracy, the initial values of the potential can be considered as independently tunable parameters, which are kept fixed at all times. Care should also be taken that the linearization implicit in the Debye-Hückel theory can be applied.

To get a qualitative idea of the effects of screening on the growth process, we first analyze the stability of a slightly deformed smooth surface by following the treatment first discussed in Ref. [17]. Let us consider a flat surface growing in the y direction between two electrodes at potentials ϕ^i and ϕ^o, respectively; the flat surface will be placed at $y=l$ and at a constant potential ϕ^i. We then deform the surface as $y^i=l+\delta\cos(mx)$, δ being very small. In the screened case the potential takes the form (setting $\phi=\phi^i$ at $y=y^i$)

$$\phi(x,y)=\phi_0(y)+E(l)\delta\exp[-(\lambda^2+m^2)^{1/2}(y-l)]\times\cos(mx)\,, \tag{2a}$$

where

$$\phi_0(y)=\frac{\phi^o\sinh[\lambda(y-l)]+\phi^i\sinh[\lambda(L-y)]}{\sinh[\lambda(L-l)]}\,. \tag{2b}$$

L is the length of the cell in the growing direction (y), and $E(l)$ is the electric field at the flat surface ($y=l$),

$$E(l)=\frac{\phi^i\cosh[\lambda(L-l)]-\phi^o}{\sinh[\lambda(L-l)]}\lambda\,. \tag{2c}$$

Then, assuming that the growth rate v is proportional to the field at the surface of the aggregate and $v=\dot{l}+\dot{\delta}\cos(mx)$, we find for the ratio between the instantaneous rates of growth of the perturbation (δ) and that of the flat surface (l) the following expression:

$$\alpha_m=\frac{\dot{\delta}/\delta}{\dot{l}/l}=\left|(\lambda^2+m^2)^{1/2}-\frac{\lambda^2\phi^i}{E(l)}\right|l\,. \tag{3}$$

In the case of no screening Eq. (3) reduces to the known result $\alpha_m=ml$. When screening is present the instantaneous growth rate depends on the potentials at the electrodes, the gap between them ($L-l$), and the screening length (λ^{-1}). Two cases should be differentiated. For $\phi^o<\phi^i$, the field at the surface of the aggregate has the same polarization of the electrodes for all values of l [$E(l)>0$]. Thus, the second term in the RHS of Eq. (3) is always negative, decreasing in absolute value as the pattern evolves. Consequently, the effect of screening will be to create dense structures which become more dilute while growing, but still resembling the Eden model.

More interesting changes are found in the case of $\phi^o>\phi^i$. In this case the most appealing feature is the

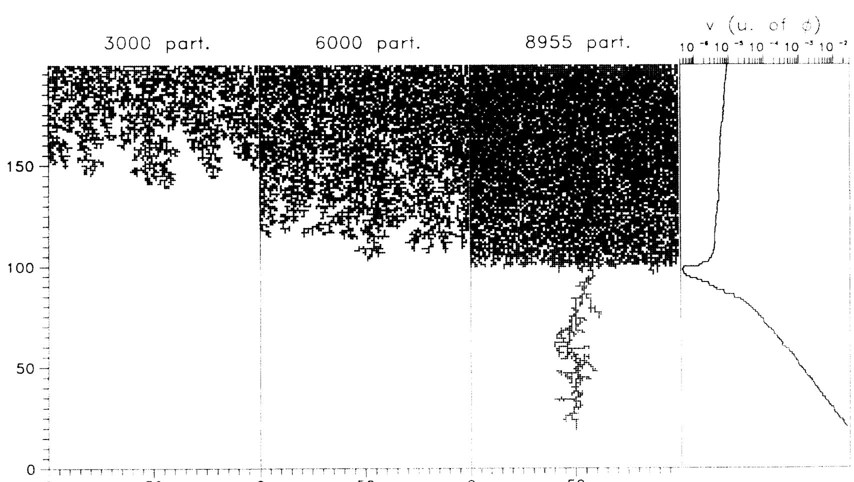

FIG. 1. Three stages of growing and velocity (average of the absolute value of electric field at the surface of the aggregate) for $\lambda^{-1}=10$, $\phi^o=1$, and $\phi^i=10^{-4}$.

possibility that $E(l)$ vanishes. For $L \gg l$ and provided that $\phi^o/\phi^i < \cosh(\lambda L)$, $E(l)$ is opposite to the polarization of the electrodes $[E(l) > 0]$. It goes to zero at a given value of l and, beyond this point, it is always negative. As a consequence, the second term in α_m is initially negative, as in the previous case, but now it increases in absolute value. As the length of the aggregate increases, and the zero of the denominator is approached, the screening term slows down perturbations of every wavelength, and the growth rate is reduced. The α_m's will vanish at different values of l, favoring dense growth. Then, at a distance which depends on the parameters of the problem (ϕ^o, ϕ^i, and the screening length λ^{-1}), $E(l)$ vanishes and the growth rate for all m's goes to ∞. Thus, beyond this point all wavelengths become unstable. Once a sharp tip develops, it will be amplified. This behavior is a consequence of the potential and its associated charge distribution. Before the transition, there is a small screening layer near the growing electrode. In the intermediate region the potential decreases to a value close to zero, to rise again near the external electrode. Hence, there are two unequal charge layers near the electrodes. Beyond the transition these two layers merge and the potential increases monotonously between the aggregate and the outer electrode.

The previous analysis fully coincides with the numerical results shown in Fig. 1. Moreover, for the parameters of that figure we have calculated from Eq. (3) that the length of the aggregate at which the transition is predicted is $l \sim 101$, in excellent agreement with the numerical results. It should be pointed out that this is a remarkable demonstration of the validity of the analysis first suggested by Mullins and Sekerka [17]. The possibility of dense growth is also well illustrated in Fig. 2, where again the transition occurs at the point predicted by the analytical study. In Fig. 1 we have also plotted the average growth speed, that is, the average of the absolute value of the field at the aggregate surface. We note that, as discussed above, the velocity vanishes at the transition. Finally we refer to the width of the thin branches that grow once the transition point has been surpassed. As is also illustrated in Fig. 2 its width increases as λ decreases (being DLA-like at scales shorter than the screening length λ^{-1}). The introduction of this new length scale is also apparent in Eq. (3). It is remarkable that screening produces dilute patterns without the need of using a growth rate proportional to a power η of the electric field different from unity, which, as remarked above, has no microscopic basis [4,6].

We have also considered under which conditions several branches may develop. Screening reduces the range of the interaction, and, therefore, should pose no problems to the growth of parallel branches. In the simulations outlined above, however, particles are added one at a time. This effect induces a sharp threshold in the velocity of growth, so that points where the fields exceed this threshold will grow and not others. As the fields, in this screened situation, have an exponential dependence on the separation between electrodes, this artificial cutoff prevents most of the front from growing. To overcome this difficulty, we have considered a front of particles that may attach stochastically at different sites without rearranging the potential at the aggregate. The results are illustrated in Fig. 3. As expected, several parallel branches can grow simultaneously.

At first glance the transition mentioned above shares many common features with the so-called Hecker transition observed in ECD. In both cases, dense and filamentary patterns develop at different times. The complexity of the real experiments greatly exceeds the simple model described here, and, presumably, other effects like diffusive growth shall also be taken into account in a complete theory. However, some aspects suggest that the main features may be well described by the present model. The transition described before is characterized by a change in the sign of the electrostatic field at the aggregate. If that takes place in the Hecker transition, a change in the charge of the chemical species being accu-

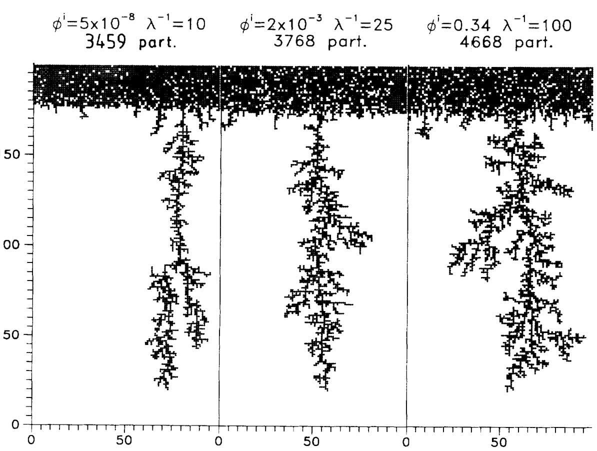

FIG. 2. Different patterns grown with $\phi^o = 1$, and several values of λ^{-1} and ϕ^i.

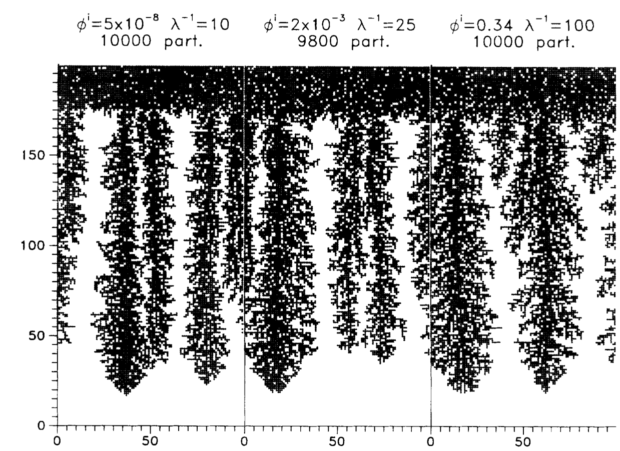

FIG. 3. Same as Fig. 2 but simultaneously attaching 50 particles at each step.

mulated near the cathode should also take place. This conclusion seems to agree with experimental findings, where a change in color, associated with a change in the material being deposited (metal oxides are replaced by metallic ions in going through the transition) has been reported [11]. A similar change in color of the solution has been identified as a change in the pH, which occurs simultaneously with the transition [14]. The change in the sign of the field observed in this work is exponentially dependent on the distance between the electrodes, while it shows a much weaker dependence on other parameters. The sharpness of the transition from dense to ramified growth depends on the range of values of l in which the a_m vary from 0 to infinity. For small values of the screened length (as compared with other typical scales), this range is small, and we expect an abrupt transition. Thus, we expect that the transition should take place in a narrow region mainly determined by the shape and dimensions of the system, in agreement with experimental findings [11]. On the other hand, the screening length (Debye length) in ECD seems to be rather small, in the range 10–300 Å [16], and therefore, much smaller than the cell size. Thus, the occurrence of the present transition in a region not too close to the outer electrode requires that $\phi^o \gg \phi^i$ (Fig. 1). This implies that, before the transition, the field near the surface of the aggregate, which, as discussed above, is opposite to the polarization of the electrodes, will be very low. Hence this electrostatic barrier can easily be overcome by cations through diffusive processes. Finally, we note that the importance of diffusion is illustrated by the fact that ECD aggregates before the Hecker transition [11] are less dense than found in this work (Figs. 1–3).

We turn to comment briefly on some further developments along the lines proposed in this work which we are currently considering. First we discuss the case of antiscreening; as remarked above this case corresponds to the presence of an ambient (or sources) of particles in DLA, and might be relevant in ECD as far as ions could be generated anywhere between the electrodes [14]. A procedure similar to that described above gives the following expression for the instantaneous growth rate:

$$a_m = \left| \theta(m^2 - \lambda^2)(m^2 - \lambda^2)^{1/2} + \frac{\lambda^2 \Phi^i}{E(l)} \right| l \,, \tag{4}$$

where θ is the step function. Now the field at the surface of the aggregate is an oscillating function of l, and, as a consequence, the growth rate also oscillates. This feature originates a behavior which is even richer than that found in the screening case. For instance, a transition similar to that described above may also take place, although in this case it occurs for $\phi^i > \phi^o$. The present analysis should be extended to growth in 2D (circular geometry), as most experiments are carried out in this geometry. Preliminary analytical studies and simulations indicate that all the results presented above also hold in the two-dimensional case. Finally we note that a finite resistivity of the aggregate also could be incorporated in the scheme proposed here: The procedure would consist in introducing a finite screening length in the aggregate.

In conclusion, we have presented an investigation of the effects of screening on growth phenomena in screened electrostatic fields. Screening strongly increases the diversity of patterns, giving rise, under certain conditions and in a very simple way, to a transition from dense to multibranched growth similar to the Hecker transition observed in ECD. Although several mechanisms might be playing a role in this transition, our results suggest that screening may be a crucial aspect of the problem.

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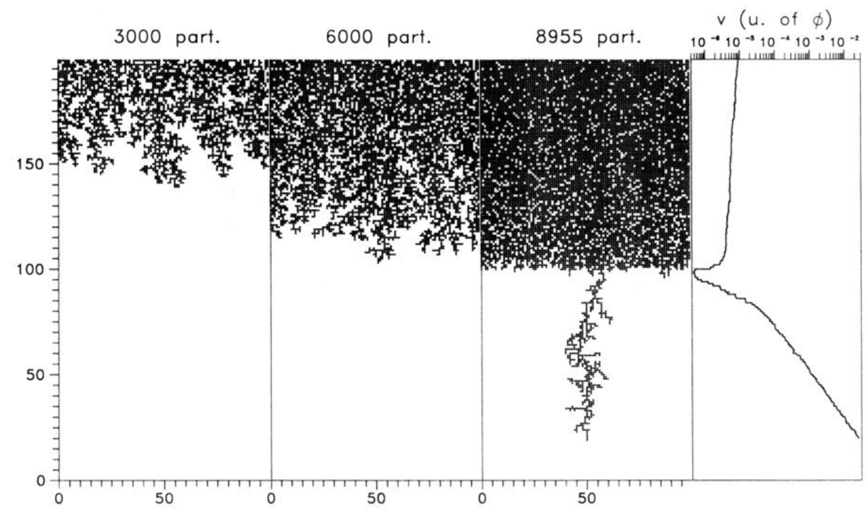

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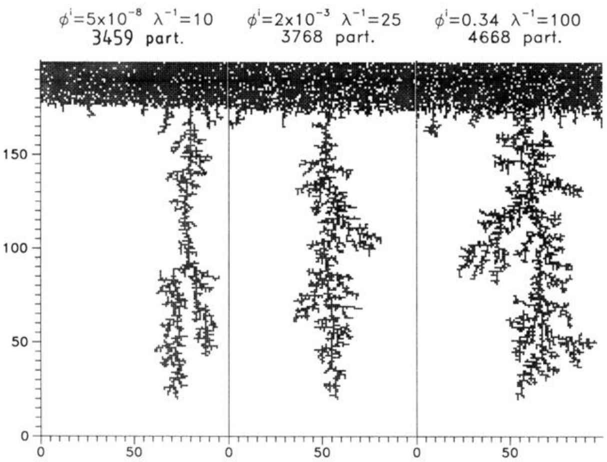

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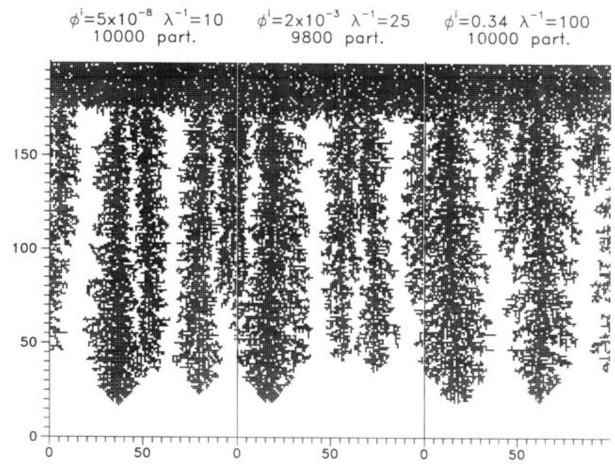

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