Stability of the Dense Radial Morphology in Diffusive Pattern Formation

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The dense radial structure is a distinct morphology which develops in many diffusive pattern-forming systems. We propose the first model to explain the stability of this structure. Stability arises in this model from the resistivity of the growth channels, which has been neglected in previous analyses. We also report excellent agreement between the predictions of our model and experimental results from two-dimensional electrochemical deposition.

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Patterns form in a wide variety of diffusive systems driven out of equilibrium. Examples of such systems include viscous fingering, amorphous annealing, dielectric breakdown, and electrochemical deposition (ECD).[1-3] In some cases (such as ECD), patterns fall into three classes: (1) fractals which resemble the clusters produced by the diffusion-limited aggregation model,[4] (2) dendritic crystals with stable tips resembling snowflakes, and (3) dense radial structures.[3] While progress has been made in our understanding of the first two morphologies, the dense radial structure has resisted analysis. In this Letter, we show that the dense radial structure is stabilized in ECD by the small but nonnegligible electrical resistance of the growing deposits.

The two-dimensional dense radial structure consists of many rough branches contained within a sharply defined circular envelope (see Fig. 1). These structures are not fractal, since they fill space uniformly. Nor are they ordinary dendritic crystals,[5] since the tips of dense radial branches are unstable. The circular envelope is not affected by the shape of the outer electrode and is remarkably robust. This is quite unexpected since the Mullins-Sekerka instability should amplify any fluctuations of the outline. Consequently, the circular envelope is perhaps the best distinguishing characteristic of the dense radial morphology.

Dense radial growth was first recognized by Sawada, Dougherty, and Gollub[3] and Grier *et al.*[2] in two-dimensional Ohmic ECD. Subsequently, similar patterns were pointed out in viscous flow and amorphous annealing by Ben-Jacob *et al.*[6] Ben-Jacob *et al.* suggest that this sort of growth arises from the combined effects of surface tension and a kinetic term in the boundary conditions at the moving interface. Linear-stability analysis based on their model accounts for the number of branches in a typical pattern, but does not explain the characteristic stability of the circular envelope in ECD. In fact, structures arising during amorphous annealing, to which our analysis does not apply, appear to have weakly unstable envelopes.

To generate dense radial aggregates, we electrodeposit metals in a system similar to one previously described.[2] Our apparatus consists of a layer of aqueous salt solution 0.013 ± 0.01 cm thick trapped between two plastic plates. The solution contacts a ring anode of the metal to be deposited 4.2 cm in radius. A copper wire with a 0.005-cm tip, introduced into the solution at the center of the ring, serves as the cathode and growth site. When a potential is applied across the cell, ions in solution plate onto the cathode to form the aggregate. By varying the applied potential and the concentration of the electrolyte, we can drive the system from fractal growth, through dense radial aggregation, to dendritic growth. For the purposes of this study, we consider only those conditions which lead to dense radial growth; see Fig. 1.

During ECD, the flux of ions onto a growing aggregate is controlled by the electrochemical potential $\mu = A(T) + kT \ln c + ze\Phi$, where $c(r)$ is the local ionic concentration, ze is the charge per ion, and $\Phi(r)$ is the electric potential.[7] Having applied a voltage V across the cell, we can define the dimensionless diffusion field $u(x) = \mu/zeV$. The total current (diffusion plus drift) is given by the gradient of u. In the quasistatic limit, we have

$$\nabla \cdot \mathbf{j} \approx \nabla^2 u = 0. \tag{1a}$$

The boundary condition at the outer electrode is

$$u(r_1) = 1. \tag{1b}$$

The boundary condition at the surface of the growing deposit would ordinarily include surface tension through a Gibbs-Thompson term. However, since the branches of dense radial aggregates are not connected at the surface, surface tension cannot play a role in large-scale pattern formation. The only contribution to the boundary condition which we consider arises from the voltage drop across the aggregate. To estimate the potential at the surface, we model the pattern as a disk of uniform effective resistivity ρ_d, with a corresponding total resistance given by

$$R(r_s) = (\rho_d / 2\pi L) \ln(r_s / r_0),$$

where L is the spacing between plates, r_0 is the radius of the cathode, and r_s is the radius of the aggregate. We

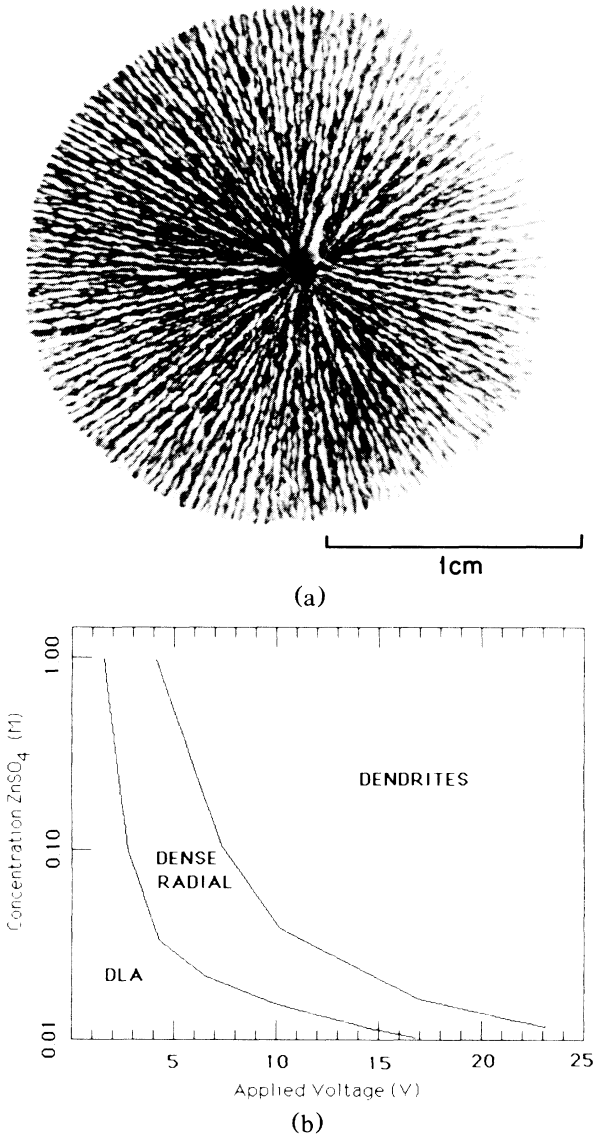

FIG. 1. (a) Zinc dense radial electrodeposit. Grown from 0.03M $ZnSO_4$ (aq) with an applied potential of 10.01 V. (b) Selected pattern as a function of applied voltage and molar concentration of $ZnSO_4$. Similar transitions are also observed in electrodeposition of copper, silver, cadmium, and lead.

assume that the current flow within the aggregate is always constrained to flow strictly radially by the filamentary branches of the aggregate. This nonlinear constraint imposed by the complex disconnected geometry of the dense radial pattern is essential for stabilization of the interface. The current density at the surface of the aggregate is related to the interfacial velocity by $j=zen_d v$, so that the potential at the interface is

$$u(r_s)=\sigma\rho_d r_s \ln(r_s/r_0)v, \tag{1c}$$

where $\sigma=zen_d/V$ and n_d is the number density of atoms in the metal.

Finally, the interfacial velocity is given by continuity of current:

$$v=(\sigma\rho_e)^{-1}(\partial u/\partial r)|_s, \tag{1d}$$

where ρ_e is the resistivity of the electrolyte.

The steady-state solution for a circular interface developing under boundary conditions (1) is a circle advancing with velocity

$$v_0(r_s)=\frac{\sigma}{r_s}\left[\rho_d \ln\left(\frac{r_s}{r_0}\right)+\rho_e \ln\left(\frac{r_1}{r_2}\right)\right]^{-1}. \tag{2}$$

Following the analysis of Mullins and Sekerka,[8] we examine the stability of this solution against a perturbation

$$r_s(t,\theta)=r_s(t)+\delta_m(t)\cos(m\theta). \tag{3}$$

We find for the instantaneous rate of growth of the perturbation, $\alpha_m=(\delta_m/\delta_m)r_s/v_0$,

$$\alpha_m=m(1-\beta)\left[\frac{1-x^{2m}}{1+x^{2m}}+m\beta\ln\left(\frac{x}{x_0}\right)\right]^{-1}-1. \tag{4}$$

Here, $x=r_s/r_0<1$, $x_0=r_1/r_0$, and $\beta=\rho_d/\rho_e$ is the ratio of the resistivity of the deposit to that of the electrolyte. When β is sufficiently large, α_m is negative for small m so that a circular profile will not develop the large-scale instabilities typical of fractal growth and will remain circular. The kinetic boundary condition introduced by Ben-Jacob *et al.*[6] to explain dense radial growth lacks the spatial dependence of (1c) and thus fails to provide the necessary stabilization. The minimum condition for circular stability is $\alpha_2=0$. This puts a lower bound on the resistivity of an aggregate necessary for dense growth:

$$\beta_{\min}\approx[1+\ln(1/x_0)]^{-1}. \tag{5}$$

In general, $\beta_{\min}<1$, so that even a relatively good conductor can form dense radial aggregates.

If the dense radial pattern were in fact solid, so that currents could flow azimuthally, the situation would map onto that of Hele-Shaw flow with finite viscosity contrast, β. In this case the pattern is unstable unless $\beta>1$. For many systems such as ECD, $\beta<1$ and stability only arises because of the detailed structure of the pattern.

Equation (4) applies directly to the case of two-dimensional dielectric breakdown where β accounts for the resistivity of the breakdown channels. Our theory may therefore explain the radially symmetric patterns with fractal dimension $D\approx 2$ observed by Niemeyer, Pietronero, and Weismann in two-dimensional gas discharges.[9]

We have noted elsewhere[10] that, in practice, dense radial electrodeposits only develop when the diffusion length in the system is considerably smaller than the radius of the cell. The above analysis holds only in the quasistatic limit. We now show that for short diffusion

lengths, resistance can still lead to stability even if β does not satisfy (5).

The diffusion length is given by $\lambda = D/v$, where D is the diffusion coefficient and v the tip velocity. λ measures the distance over which the electrochemical potential is affected by the growing deposit and correlations between growing regions separated by distances greater than λ are suppressed. In the limit $\lambda \ll r_1$ (our measurements[10] give $\lambda < 0.1$ cm whenever dense radial growth occurs), the scale invariance characteristic of fractals cannot arise.[11] Short diffusion lengths can therefore explain the observed uniform areal density of the aggregates, although they do not lead to stable circular envelopes by themselves.

In the short-diffusion-length limit, the electrochemical potential approximately[12] satisfies the diffusion equation instead of the Laplace equation,

$$D\nabla^2 u = \partial u/\partial t. \tag{6a}$$

The boundary condition $u(r_1) = 1$ must be applied far in front of the advancing plane

$$u(r_s + n\lambda) = 1, \tag{6b}$$

where $n \gg 1$ and r_s is the position of the plane. The boundary conditions at the moving interface are, as before,

$$u(r_s) = \sigma\rho_d r_s v, \tag{6c}$$

$$v = (\sigma\rho_e)^{-1}(\partial u/\partial r)|_s, \tag{6d}$$

where ρ_e is now to be expressed in terms of D by the Nernst-Einstein relation. In (6c) we have absorbed the logarithm of (1c) into ρ_d.

Zener[13] has given a solution to (6) for the case $u(r_s) = u_s = \text{const}$:

$$u(r) = 1 + \frac{(u_s - 1)\Phi(x/(Dt)^{1/2})}{\Phi(\zeta)}, \tag{7a}$$

$$\Phi(z) = \int_z^\infty \exp(-x^2/4)\,dx. \tag{7b}$$

This solution corresponds to a plane advancing with

$$r_s = \zeta(Dt)^{1/2}. \tag{7c}$$

Note that in our case we also have $u_s = \text{const}$ because

$$u(r_s) = \sigma\rho_d\zeta^2 D/2. \tag{8a}$$

This implies, with use of (6d), a self-consistency relation for ζ:

$$2(1 - u_s) = D\sigma\rho_e\zeta\Phi(\zeta)\exp(\zeta^2/4). \tag{8b}$$

We apply a perturbation of wave number k to the interface after having let it grow to size $r_s = \zeta(Dt_0)^{1/2}$:

$$r_s(t) = r_s + \delta_k(t)e^{iky}. \tag{9}$$

The rate of growth of the perturbation is

$$\alpha_k = qr_s[(1-\beta) - 1/q\lambda][1 + qr_s\beta]^{-1}, \tag{10a}$$

where q satisfies

$$q^2 - q/\lambda - k^2 = 0. \tag{10b}$$

In the limit of short diffusion lengths, (10) shows that the flat profile of the advancing plane is stable for all wave numbers smaller than k_c given by

$$k_c\lambda = [\beta^{-1} - 1]^{-1/2}. \tag{11a}$$

We can approximate the corresponding stability condition in the circular growth case by

$$m_c = k_c r_s. \tag{11b}$$

The condition for stabilization of the circular envelope, $m_c \geq 2$, determines the minimum resistivity sufficient for dense radial growth,

$$\beta_{\min}(\lambda) \approx [1 + (r_s/2\lambda)^2]^{-1}. \tag{11c}$$

Short diffusion lengths enhance the stabilizing effect of a deposit's resistivity.

One result of (11) is that the planar solution is always unstable for $\beta < 1$ in the long-diffusion-length limit. In this limit, however, the planar geometry is not a good representation for our two-dimensional system. Under these conditions, when $\lambda > r_1$, (4) must be used instead. The additional stabilization in the radial case arises from the $1/r$ dependence of the current density which is not present in the planar case.

The condition for stable dense radial growth set by (11c) is observed to be met by all dense radial aggregates grown by ECD. To apply our result to ECD, we have experimentally determined β from the deposition current, $i(r_s)$, by applying the relation

$$i_0/i(r_s) = (1-\beta)\ln(r_1/r_s) + \beta\ln(r_1/r_0), \tag{12}$$

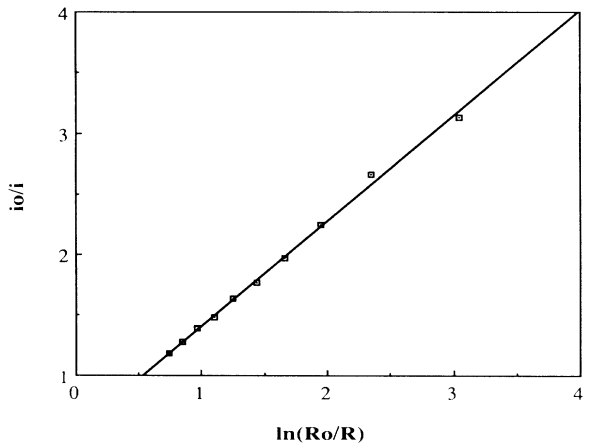

FIG. 2. Deposition current vs radius of aggregate plotted according to Eq. (12). Experimental error bars are too small to be seen at the resolution of the graph. This run produced the aggregate shown in Fig. 1. A linear least-squares fit to the data indicates $\beta = 0.132$.

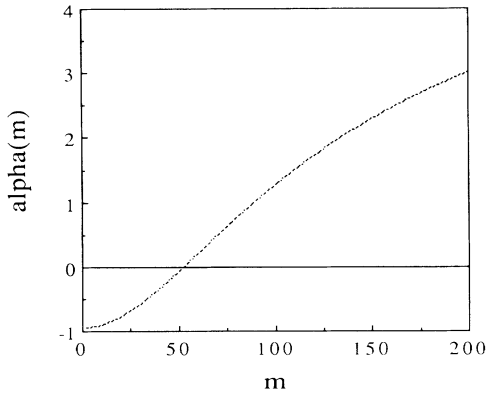

FIG. 3. Rate of growth of perturbations vs mode number m, for $\beta=0.132$ and $\lambda=0.008$ cm.

where $i_0=2\pi LV/\rho_e$. We have estimated ρ_e and D from standard tables and have checked these values by measurement.[14] Figure 2 shows data from the experimental run which produced the deposit in Fig. 1. The excellent fit to the data by (12) supports the assumed logarithmic dependence of the resistance of the deposit; the slope of the fitted line gives $\beta=0.132$. Under the conditions of this run ($0.03M$ $ZnSO_4$, 10.01 V), the diffusion length is measured[10] to be 0.008 cm at $r_s=1.0$ cm, and (11c) gives $\beta_{\min}\approx 0.0003$. Because $\beta>\beta_{\min}$, the aggregate is sufficiently resistive to be stabilized by our mechanism. The measured resistance is orders of magnitude greater than the volume-fraction–weighted resistance of the bulk metal because the current-carrying filaments have cross-sectional areas of only $\simeq 0.01$ μm^2 as determined by scanning electron microscopy examination. In Fig. 3 we plot the growth rate α_m, calculated with the measured value of β. For small m, α_m is indeed negative, in agreement with the observation that the envelope in Fig. 1 is circular to within 5% for $m<20$.[15] We obtain similar agreement with theory over the entire range of experimental conditions, as well as in other metals, including copper, cadmium, silver, and lead.

These observations suggest that the dense radial morphology arises in ECD from the resistivity of the growth channels. For two-dimensional diffusive growth, our theory predicts that a circular envelope will be stable if the relative resistivity of the growth channels exceeds $\beta_{\min}$. This threshold value is given by (5) for systems governed by the Laplace equation, and by (11) in the short-diffusion-length limit. We suggest that if either of these conditions is met, then the dense radial pattern should emerge.

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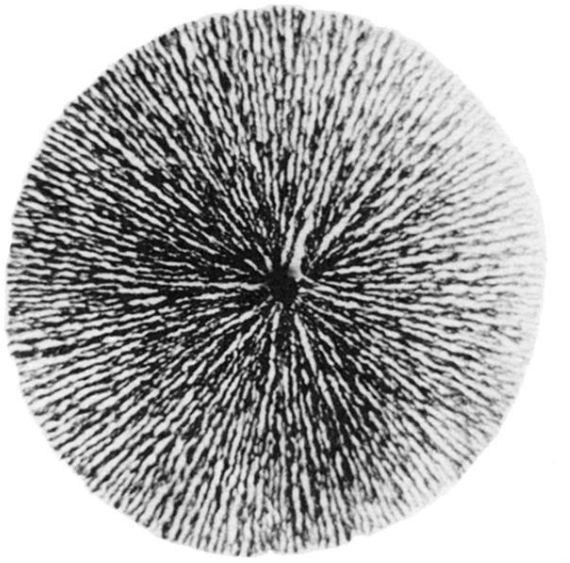
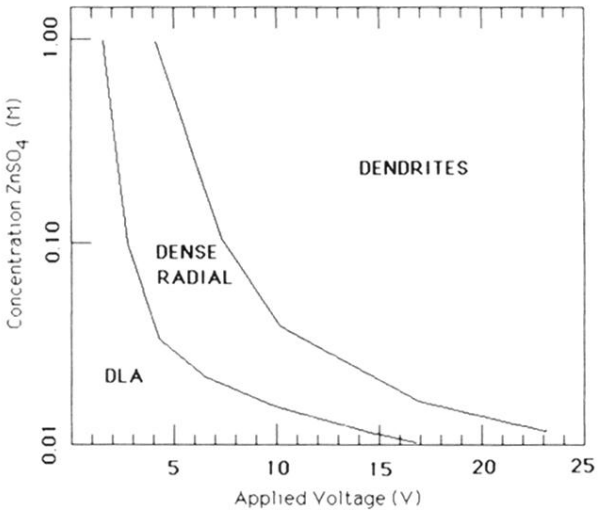
[14]*CRC Handbook of Chemistry and Physics*, edited by R. C. Weast and S. M. Selby (CRC Press, Cleveland, OH, 1975), 56th ed., pp. D-218–D-267. We estimate the dc conductivity of electrolytic solutions by extrapolation of the ac conductivity of solution in a cell 1.0 cm long of cross-sectional area 0.90 mm^2 measured with an impedance bridge.

[15]Distortions from circularity were measured as rms deviations from the average radii of the envelopes with a resolution of 0.1 mm by means of an Oculus-200 image-processing board in a personal computer.



(a)



(b)

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