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Evolution of the space-charge layer during electrochemical deposition with convection

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We study the effect of convection on the concentration profiles in electrolytic cells during electrochemical deposition without a supporting electrolyte. We give theoretical evidence that convection decreases the size of the space charge on the cathodic side during fast electrochemical deposition. This effect may provide a limiting amplitude of the convective motion.

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I. INTRODUCTION

Much attention has been devoted recently to the deposition of aggregates from a solution of a salt of a metal, with supporting electrolyte [1–25]. Initially, these studies aimed at validating the diffusion-limited aggregation [26,27] model of Witten and Sander, a numerical model of ramified fractal growth. However, the electrochemical aspects of the growth were found to play a decisive role and the complete problem of the deposition of a metal from a solution ($C \sim 0.001-1$ mol l^{-1}) of a salt of a metal (e.g., $CuSO_4$, $ZnSO_4$) and under high current densities ($J \sim 1-20$ mA cm^{-2}) had to be addressed. Chazalviel [16] has proposed recently an analytical and a numerical solution of this problem which takes into account the displacement of the ions in the solution due to both electric migration and diffusion. The solution proposed by Chazalviel leads to the conclusion that there must be a large charged region, which is now generally called the Chazalviel layer, near the cathode, or near the tips (if there are any) of the deposit. This model gives a first and very deep insight into the growth mechanism. However, one important feature is not incorporated into this model: electroconvection. It has been shown by Fleury, Chazalviel, and Rosso [18,19] that a convective, or even turbulent, motion can be expected in the vicinity of the cathode, or near the deposit, because of this positive charge which is predicted to exist in the active zone of the deposit. But this convective motion leads now to an additional transport mechanism—the advection of the ions in the fluid flow. We will show in the following that incorporating convection to Chazalviel's model leads to a decrease of the size of the charged layer.

In this paper, we will not address the full two-dimensional case around a growing deposit; rather, following Chazalviel [16], we shall first study the effect of convection on the smooth deposition along a linear cathode. While this may seem a rather artificial problem, we must recall that addressing this situation leads to a clear understanding of the transport of ions in a complicated, though soluble, case. The interpretation of the corresponding features along growing tips is then made easier. As a matter of fact, this paper shall be more easily read with Chazalviel's paper [16] in hand. The paper is divided as follows: in Sec. II we shall present an analytical derivation of the concentration profiles, when convection is included, for an electrochemical deposition which does not change the shape of the electrode (smooth deposition case). In Sec. III A we present the corresponding results for the case of growth at a constant speed (the recession speed of the anions [9,14,16]) of a uniform sheet of metal. Finally, in Sec. III B, we discuss some consequences that can be extrapolated to the actual deposition of a ramified pattern.

II. SMOOTH DEPOSITION IN A LAMINAR FLOW

A. Analytical derivation in the general case

We will now study the following physical situation. We consider a rectangular cell of length L, with linear electrodes (cathode at $x=0$ and anode at $x=L$; see Fig. 1). We suppose that this cell is filled with a salt of a metal (binary electrolyte) and that a potential difference U is applied between the electrodes. Concerning convection, it is assumed that a constant flow $-v\mathbf{i}$ goes through the cell. This flow is oriented from the anode toward the cathode. This flow can either be a forced flow, or a gravity-driven flow, or, as argued below, an electroconvective motion due to the positive charge which will eventually be proven to exist near the cathode. However, for the time being, we simply impose the existence of this laminar flow.

The first step is to write down the equations of transport in the cell. The motion of the ions is due to diffusion (the $D\Delta C$ term), migration [the $\mu\,\mathrm{div}(\mathbf{E}C)$ term], and advection (the $\mathbf{v}\cdot\nabla C$ term):

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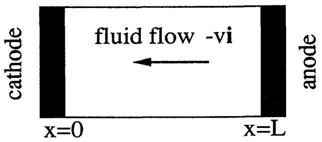

FIG. 1. Scheme of the cell for the model discussed in Sec. II. The fluid flow is a constant flow going from the anode towards the cathode. The fluid flow is supposed not to bring ions in at the anode nor to take the ions away behind the cathode.

$$\frac{\partial C_c}{\partial t}=D_c\Delta C_c-\mu_c\mathbf{E}\cdot\nabla C_c-\mu_c C_c\,\mathrm{div}\mathbf{E}-\mathbf{v}\cdot\nabla C_c\ , \qquad (1)$$

$$\frac{\partial C_a}{\partial t}=D_a\Delta C_a+\mu_a\mathbf{E}\cdot\nabla C_a+\mu_a C_a\,\mathrm{div}\mathbf{E}-\mathbf{v}\cdot\nabla C_a \qquad (2)$$

$$\mathrm{div}\mathbf{E}=e(z_c C_c-z_a C_a)/\epsilon\epsilon_0\ , \qquad (3)$$

where the D's are diffusion constants, the C's concentrations, and the μ's mobilities; the subscript a stands for anion and the subscript c stands for cation. Diffusion constants and mobilities are supposed to not depend on concentration. z_c and z_a are the charge numbers of the cations and the anions, respectively. $\mathbf{E}$ is the electric field, $-e$ the charge of the electron, and ϵ the relative dielectric constant of the solvent. We now suppose also that the deposition is smooth, so that the shape of the cathode does not change (i.e., it remains linear and flat). Since we are interested here in the one-dimensional problem of the concentrations and electric field across the cell, we can write the equations as a function of the distance x to the cathode:

$$\frac{\partial C_c}{\partial t}=D_c\frac{\partial^2 C_c}{\partial x^2}-\mu_c E\frac{\partial C_c}{\partial x}-\mu_c C_c\frac{\partial E}{\partial x}+v\frac{\partial C_c}{\partial x}\ , \qquad (4)$$

$$\frac{\partial C_a}{\partial t}=D_a\frac{\partial^2 C_a}{\partial x^2}+\mu_a E\frac{\partial c_a}{\partial x}+\mu_a C_a\frac{\partial E}{\partial x}+v\frac{\partial C_a}{\partial x}\ , \qquad (5)$$

$$\frac{\partial E}{\partial x}=e(z_c C_c-z_a C_a)/\epsilon\epsilon_0\ . \qquad (6)$$

(In this one-dimensional problem, the fluid flow is constant through the cell, so the Navier-Stokes equation is trivially satisfied.) We can also write the fluxes W of anions and cations:

$$W_c=-D_c\frac{\partial C_c}{\partial x}+\mu_c E C_c-vC_c\ , \qquad (7)$$

$$W_a=-D_a\frac{\partial C_a}{\partial x}-\mu_a E C_a-vC_a\ , \qquad (8)$$

and the current density

$$J=z_a eW_a-z_c eW_c\ . \qquad (9)$$

Following Chazalviel, we will soon make a two-zone approximation; however, one can derive from Eq. (8) a relation between the potential and the concentration of anions which is valid throughout the cell. Indeed, since the anions do not participate in the electrochemical process, the anions must be frozen in the stationary state. Note that this implies also that the model does not allow the flow to carry anions away behind the cathode. Writing $W_a=0$ we have

$$0=-D_a\frac{\partial C_a}{\partial x}-\mu_a C_a\frac{\partial V}{\partial x}-vC_a\ , \qquad (10)$$

which implies, with help of the Einstein relation $D_a/\mu_a=kT/z_a e$,

$$C_a(x)\sim\exp\{(z_a e/kT)[V(x)-vx/\mu_a]\}\ . \qquad (11)$$

We now keep this relation in mind and make a two-zone approximation. Following Chazalviel, we suppose that there exist two zones: Zone I is a layer close to the cathode, where the concentration of anions is neglected, and where there will exist an excess of positive charges. In zone I, the potential is expected to vary rapidly because of this excess of charges. Zone II is a region further from the cathode and which extends up to the anode, where the solution is expected to be quasineutral. In this region, the potential should vary much less steeply. (The curvature of the potential will be negligible.) Following Chazalviel, the frontier between the two zones is designated by x_I. This location of the border, which defines the thickness of the charged layer, is a constant in Chazalviel's model, while it will here depend on the fluid speed v. Now, we have separated the problem into two problems: In zone I we have

$$W_c=-D_c\frac{\partial C_c}{\partial x}+\mu_c E C_c-vC_c\ , \qquad (12)$$

$$J=z_c eW_c\ , \qquad (13)$$

$$\frac{\partial^2 V}{\partial x^2}=-ez_c C_c/\epsilon\epsilon_0\ . \qquad (14)$$

[In this zone $W_a=0$ and $C_a(x)=0$, of course.] In zone II we have

$$z_c C_c=z_a C_a\ , \qquad (15)$$

$$W_c=-D_c\frac{\partial C_c}{\partial x}+\mu_c E C_c-vC_c\ , \qquad (16)$$

$$J=z_c eW_c \qquad (17)$$

(and $W_a=0$).

It turns out that the set of equations in zone I allows us to calculate a relation between the size of the space-charge region and J, while the set of equations in zone II allows us to calculate J, as we now show.

In zone I, Eqs. (12) and (13) give

$$\frac{dV}{dx}=-J/\mu_c z_c eC_c-v/\mu_c\ , \qquad (18)$$

This implies, after differentiation by x and neglecting diffusion,

$$\frac{d^2V}{dx^2}=-[J/\mu_c z_c e]dC_c/C_c^2 \qquad (19)$$

(the fluid velocity disappears because it is a constant; physically, it means that the fluid velocity, being a constant, cannot change the curvature of the potential). By equating this equation with the Poisson law one finds an equation which contains only the concentration of cations:

$$[1/C_c^3]dC_c = -z_c^2 e^2 \mu_c / \epsilon\epsilon_0 J \ . \tag{20}$$

This gives

$$1/C_c^2(x_I) - 1/C_c^2 = -[2z_c^2 e^2 \mu_c / \epsilon\epsilon_0 J](x - x_I) \ . \tag{21}$$

In principle, one can now derive C_c from this equation. Then C_c can be replaced by its expression inside the Poisson law. Integrating twice the Poisson law will give the potential inside the charged layer, as a function of the distance to the frontier between zone I and zone II. However, this approach leads to very complicated algebra, because the expression of C_c is not very simple. Instead, we can do a further simplification, which consists in neglecting the term $1/C_c^2(x_I)$ in Eq. (21). This term can be neglected, because we expect to have "large" concentrations of cations in the charged layer. The Avogadro number transforms this concentration of cations into a very large number indeed. By doing so, we find an expression of C_c which is

$$C_c = \{\epsilon\epsilon_0 J / 2z_c^2 e^2 \mu_c (x - x_I)\}^{-1/2} \ . \tag{22}$$

This expression is *singular* at $x = x_I$. This singularity comes from identifying ∞ and, say, 10^{15}. It could be removed by using the more accurate expression $C_c = \{\epsilon\epsilon_0 J / 2z_c^2 e^2 \mu_c (x - x_I)\}^{-1/2} C_c(x_I) [2z_c^2 e^2 \mu_c (x - x_I) / \epsilon\epsilon_0 J + C_c^2(x_I)]^{-1/2}$, which is complicated indeed. By integrating twice Eq. (22), one finds

$$V = V(x_I) - \tfrac{2}{3}(-2J/\mu_c \epsilon\epsilon_0)^{1/2}(x_I - x)^{3/2} \ . \tag{23}$$

As we see, the singularity of C_c does not induce a singularity in V, because, while the concentration is singular at x_I, the total number of atoms is not. Replacing $C_c(x_I)$ by ∞ amounts to replacing the integral up to $C_c(x_I)$ by an integral up to ∞. Since the integral is of a converging type, and since $C_c(x_I)$ is very large, the difference between the two is negligible.

The two-zone approximation implies that the potential at x_I is almost equal to the potential at L then the potential in the charged layer is

$$V = V(L) - \tfrac{2}{3}(-2J/\epsilon\epsilon_0 \mu_c)^{1/2}(x_I - x)^{3/2} \ . \tag{24}$$

Writing that the potential is zero at the cathode implies that

$$-x_I^3 J = (3U/2)^2 \epsilon\epsilon_0 \mu_c / 2 \ , \tag{25}$$

where U is the potential difference between the electrodes. This equation is exactly the same as the one obtained by Chazalviel [Eq. (27) of Ref. [16]] because the derivative of the fluid speed is zero. We took advantage of this calculation to explain the origin of the singularity in C_c which appears in Chazalviel's model and is often criticized.

By studying the charged layer, we have just derived Eq. (25) linking the size of the charged region to the current. We now proceed to zone II in order to find a second relationship, which will give J. In this zone, the calculation will be somewhat different than Chazalviel's. Equation (16) gives

$$-W_c = -J/z_c e = D_c \frac{\partial C_c}{\partial x} + \mu_c C_c \frac{\partial V}{\partial x} + vC_c \ , \tag{26}$$

but Eq. (10) gives also a relationship between V and C_a, and C_a is simply equal to $(z_c/z_a)C_c$. Putting together Eqs. (26) and (10) then gives

$$-J/z_c e = (1 + z_c/z_a) D_c \frac{\partial C_c}{\partial x} + (1 + \mu_c/\mu_a) vC_c \ . \tag{27}$$

This is the equation satisfied by the concentration of cations in the quasineutral region (zone II). This equation differs from the one obtained by Chazalviel because of the presence of the last term, which is linear in C_c. Integrating this equation gives

$$z_c C_c = z_a C_a = -\frac{J}{e\left[1 + \dfrac{\mu_c}{\mu_a}\right]v} \left\{ 1 - \left[\exp\left[\frac{\left[1 + \dfrac{\mu_c}{\mu_a}\right]v}{\left[1 + \dfrac{z_c}{z_a}\right]D_c}(x - x_I) \right] \right] \right\} . \tag{28}$$

This gives the concentration of anions in the bulk. One should note that right at $x = x_I$, the concentration of anions vanishes. This is normal, since we suppose that the Chazalviel layer is completely depleted of anions. Now, this makes the concentration of cations also equal to zero by virtue of the equality on the left-hand side of Eq. (28). This may seem shocking, since we have shown previously that the concentration of cations diverges at $x = x_I$ and since we have argued that, while not being infinite, it was still "very large." How can one paste a solution with $C = 0$ (at $x = x_I^-$) to a solution with $C = \infty$ (at $x = x_I^+$) (as Chazalviel does)? In fact, there is no real problem. The very large concentration in the charged layer is a very large number (of order, say, 10^{15}) with respect to the integration over the concentration while the "very small" (exactly zero right at $x = x_I^+$) concentration in the quasineutral region is a very small value compared to the bulk concentration (which is about 10^{21}). As a consequence, there is no problem in pasting the solution with $C = 10^{15}$ (considered as $\sim\infty$) on the $x = x_I^-$ side with $C=10^{15}$ (considered as ~ 0) on the $x=x_I^+$ side.

Now one obtains a second equation by writing down that the total number of anions is unchanged. This means that

$$\int_{x_I}^{L} C_a dx = C_0 L \ . \tag{29}$$

One should note that the number of cations is not conserved. In the stationary state, the cell is positively charged. The excess of cations is produced by the dissolving anode. This positive charge is responsible for the curvature of the potential along the cell. Global electroneutrality is achieved by means of a negative charge at the cathode, but on the metal side, composed of electrons.

The integration of the concentration of anions yields

$$\frac{J}{z_c eMv}\left\{L-x_I+D_c\frac{Z}{Mv}\left\{\exp\left[\frac{Mv}{ZD_c}(L-x_I)\right]-1\right\}\right\}=C_0 L \tag{30}$$

in which, for clarity, we have defined $M=1+\mu_c/\mu_a$ and $Z=1+z_c/z_a$. One can expect the space-charge region to be very narrow. Hence we can write $L-x_I\sim L$, which gives the current density through the cell, in the stationary regime, as a function of the fluid speed v:

$$J\approx z_c eMv\left\{L+D_c\frac{Z}{Mv}\left\{\exp\left[\frac{Mv}{ZD_c}L\right]-1\right\}\right\}^{-1}C_0 L \ . \tag{31}$$

We have represented in Fig. 2 the concentration profiles as a function of the fluid speed. The curve $v=0$ corresponds to the case first treated by Chazalviel. In the case $v=0$, the concentration of anions is almost linear across the cell. When the fluid speed is turned on, the concentration profile changes and has a shoulderlike shape. The Chazalviel layer, which is very small with the usual values of the electrochemical parameters, does not appear in the figure.

B. Case of very small fluid speed

A linear expansion dow to the *third order* of the equation shows that the current density is

$$J\approx -2eD_cZ(C_0/L)\left[1+\frac{LM}{3z_aD_c}v\right]\approx J^0\left[1+\frac{LM}{3z_aD_c}v\right] , \tag{32}$$

where J^0 is Chazalviel's value. As one can see, the current increases if there is an additional fluid speed. Since the current density is larger, x_I will be smaller, according to Eq. (26), which gives, in the limit of small fluid speeds,

$$x_I\approx x_I^0\left[1-\frac{LM}{9z_aD_c}v\right] , \tag{33}$$

where x_I^0 is the length of the space-charge region obtained by Chazalviel.

The fact that the current increases, while not surprising, is not completely trivial. Since anions and cations have opposite charge, one could naively think that a constant flow would give an overall null effect. However, in the stationary regime, the anions must be frozen. This imposes a gradient of concentration which balances the sum of the electric migration and of the advection of the anions. The advection term implies a flatter profile of anions than in the case without advection, because the advective term is opposite to the migration term. Turning now to the cations, we see that the advective term, the diffusive term, and the migration term add up. While the advective term has a tendency to increase the flux of cations, the diffusive term is smaller than in the case without advection. The interplay of these three effects gives Eq. (26), which, by integration, gives the profile of both cations and anions in the bulk. The final value of the current is then found by writing down the conservation of anions. All in all, the fact that the current increases is not obvious.

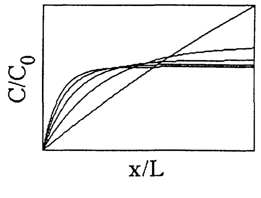

FIG. 2. The concentration of anions in the cell, as a function of the fluid speed, for typical values of the concentration and the applied voltage. When there is no fluid flow, the concentration varies linearly in the cell, as in Chazalviel's model (without convection). When the fluid flow is incorporated in the model, the shape of the concentration is no longer linear. Also, the size of the space charge (which is very small with the value $C=10^{18}$ taken here) decreases when v increases.

C. Case of very fast fluid flow

It is interesting, as a side result, to investigate the limit of very fast flow. In this limit, the approximations of Chazalviel's model cannot hold. The field which is found in the bulk of the solution, which is at most of U/L (where U is of order 10 V and L is of order 1 cm) can counterbalance an advective motion up to an advective term equal in magnitude to $\mu U/L$ only. Also, the "Fick translation" of the ions is very weak, and it is impossible that concentration gradients should be able to counterbalance such a large advective term. Hence the conclusion is that *there cannot be anions in the bulk of the solution.* While this may sound absurd, it is in fact very physical. A huge field speed will simply pack the anions and the cations along the cathode, regardless of diffusion and migration (let us recall that in the situation described here, no ions are produced at the anode, nor brought in by the fluid flow, and the ions cannot be taken away by the flow through the cathode; in this rather artificial situation, one can imagine a small demon at the cathode allowing the water to flow away, but not the ions). There will remain a very small excess of positive charges in the bulk of the cell, composed of cations which are carried from the dissolving anode to the cathode by the sum of the advective motion and of the migration (diffusion will be negligible there). This excess of positive charges will be responsible for the shape of the potential, which will go from a value of zero near the cathode to the value $V(L)=U$ at the anode. [In fact, one should incorporate the Nernst contribution to the potential and take the potential at the cathode to be $-(kT/ze)\ln(C/C_0)$ and at the anode $U-(kT/ze)\ln(C/C_0)$, but these corrections are rather minor and can be sacrificed here on the altar of clarity.] In order to determine the shape of the potential and the value of the current we first must write that J is the sum of the current density of electric origin and the current density due to advection of the ions,

$$J=-\left[v+\mu_c\frac{\partial V}{\partial x}\right]C_c(x)\ , \tag{34}$$

and Poisson's law,

$$\frac{\partial^2 V}{\partial x^2}=-z_c eC_c(z)/\epsilon\epsilon_0 \tag{35}$$

(recall that with our notations, $e>0$ and $J<0$). The physical problem is to find a distribution of charges and a potential such that the flux (advection plus migration) is conserved while the potential goes from 0 to U. In order to achieve that, the former equations imply to solve the following differential equation:

$$\frac{\partial^2 V}{\partial x^2}\left[v+\mu_c\frac{\partial V}{\partial x}\right]=z_c eJ/\epsilon\epsilon_0 \text{ with } V(0)=0\ ,\ V(L)=U\ . \tag{36}$$

A standard technique consists in defining $u=\partial V/\partial x$, hence

$$vu'+\mu_c uu'=z_c eJ/\epsilon\epsilon_0\ , \tag{37}$$

which gives first

$$u^2+2uv/\mu_c-2z_c eJx/\mu_c\epsilon\epsilon_0+A=0\ , \tag{38}$$

hence

$$V(x)=-\frac{v}{\mu_c}x-\frac{\mu_c\epsilon\epsilon_0}{2z_c eJ}\left[\left[\frac{v}{\mu_c}\right]^2+A-\left[\frac{2z_c eJ}{\mu_c\epsilon\epsilon_0}x\right]\right]^{3/2}+\frac{\mu_c\epsilon\epsilon_0}{2z_c eJ}\left[\left[\frac{v}{\mu_c}\right]^2+A\right]^{3/2}\ . \tag{39}$$

We have two unknown quantities: the constant A and the current density J [we have readily taken into account that $V(0)=0$]. In order to determine these we first use the fact that the concentration of cations must be infinite near the anode. This is so because the anode is supposed to be perfectly soluble: it is an infinite source of cations. Note that the condition that the concentration is infinite implies that, at the anode, the drift velocity is exactly opposite to the drift flow ($\mu_c E=v$). The second condition which we must use is $V(L)=U$.

The condition $C(L)=\infty$ implies

$$A=-(2z_c eJL/\mu_c\epsilon\epsilon_0)-(v/\mu_c)^2 \tag{40}$$

and $V(L)=U$ implies

$$J=-(\mu_c\epsilon\epsilon_0/L2z_c e)(U/L+v/\mu_c)^2\ . \tag{41}$$

This gives the following shapes of the potential and the concentration of cations:

$$V(x)=-\frac{v}{\mu_c}x+\left[\frac{U}{L}+\frac{v}{\mu_c}\right]\left[L-L\left[1-\frac{x}{L}\right]^{3/2}\right]\ , \tag{42}$$

$$C(x)=\frac{3\epsilon\epsilon_0}{4Lz_c e}\left[\frac{U}{L}+\frac{v}{\mu_c}\right]\left[1-\frac{x}{L}\right]^{-1/2}\ , \tag{43}$$

which are shown in Fig. 3. Let us mention that this kind of equation often arises in the study of current injections and plasma injections into insulators [28].

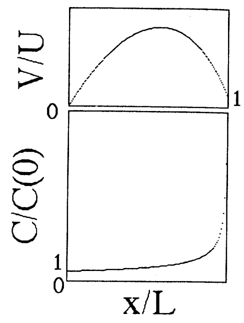

FIG. 3. The potential and the concentration of cations across the cell, in the case of a very fast fluid flow ($v=0.4$ cm s^{-1}). In this instance, the concentration must be taken as infinite near the anode, because the dissolution of the anode is, in theory, instantaneous.

III. DISCUSSION OF THE TWO-DIMENSIONAL CASE

A. Case of a flat deposit

We now address the following situation: we suppose that a smooth and uniform deposit grows. By smooth and uniform, we mean that the deposit is like a flat uniform sheet with a straight edge and not like a ramified pattern (see Fig. 4). The case of the ramified pattern will be discussed in the next paragraph of this section. We

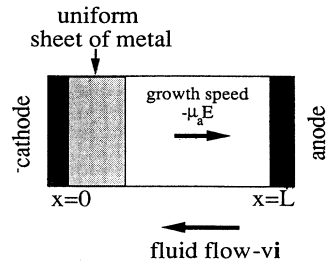

FIG. 4. Scheme of the cell and the deposit for the case of smooth and uniform deposition. The deposit is a flat uniform sheet with a straight edge. There is a charged zone along the edge, where the deposition process is under way.

suppose also that the deposit grows at a constant speed, which is $-\mu_a \mathbf{E}_0$ ($\equiv v_a$, the recession speed of the anions [9,14,16,17] when there is no flow). We know experimentally, and we will assume it to be true here too, that there exists a potential drop δU of order 1 V in the vicinity of the edge (the so-called active zone). Concerning convection, we assume that there exists a constant flow, with a speed $-\mathbf{vi}$, coming from far ahead towards the deposit and flowing away in the rear zone of the deposit. This situation is very much like Sec. III B of Chazalviel's paper, except that convection was not taken into account there. We suppose that the solution is not perturbed far away, so we take the concentrations and the field far away to be equal to their bulk values C_0 (of order 10^{-2} mol/l) and $\mathbf{E}_0$ (of order 10 V/cm).

As in Sec. II, there will be a charged zone which advances in the solution with the edge of the deposit. In order to find the size of the space charge, it is easier to analyze the problem in the moving frame of the edge of the deposit and incorporate a new "advective" term in the transport of the ions, which corresponds simply to the displacement of the moving frame. The equations are then very much like Eqs. (4)–(6), they read

$$\frac{\partial C_c}{\partial t}=D_c\frac{\partial^2 C_c}{\partial x^2}-\mu_c E\frac{\partial C_c}{\partial x}-\mu_c C_c\frac{\partial E}{\partial x}+(v+v_a)\frac{\partial C_c}{\partial x}\ , \tag{44}$$

$$\frac{\partial C_a}{\partial t}=D_a\frac{\partial^2 C_a}{\partial x^2}+\mu_a E\frac{\partial C_a}{\partial x}+\mu_a C_a\frac{\partial E}{\partial x}+(v+v_a)\frac{\partial C_a}{\partial x}\ , \tag{45}$$

$$\frac{\partial E}{\partial x}=e(z_c C_c-z_a C_a)/\epsilon\epsilon_0\ . \tag{46}$$

Of course, the boundary conditions are not the same; they become here $dC_c(0)/dx=0$ (diffusion of cations negligible near the deposit), $W_a(0)=0$ (no flux of anions, i.e., the anions are frozen in the moving frame), and $V(0)=-(kT/z_c e)\ln[z_c C_c(0)/C_0]$ (Nernst potential on the boundary). Following Chazalviel, and Sec. II, the integration of this set of equations gives

$$C_a(x)\sim\exp\{(z_a e/kT)[V(x)-(E_0+v/\mu_a)x\}\ . \tag{47}$$

(Mind that with our conventions, E_0 and v are of the same sign, so their contributions add up; in the moving frame the motion of the liquid is the sum of the absolute motion $\mathbf{v}$ and the relative emotion $\mu_a \mathbf{E}_0$; we have written the absolute motion $-v\mathbf{i}$ and the field $\mathbf{E}_0=-E_0\mathbf{i}$.) The expression of the concentration in the quasineutral region is similar to Eq. (28), after replacing v by $\mu_a E_0+v$. Note that in the case discussed in Sec. II the current density J comes out of the calculation by imposing that the number of anions is conserved; in the case discussed here it is fixed by the boundary condition

$$z_c C_c=z_a C_a$$
$$=C_0\left[1-\exp\left[\frac{M}{ZD_0}(\mu_a E_0+v)(x-x_I)\right]\right]\ . \tag{48}$$

This can also be obtained from Chazalviel's result [Eq. (50) of Ref. (16)] after replacing $\mu_a E_0$ by $\mu_a E_0+v$. Next, the potential is still given by

$$V=\delta U-E_0 x+(kT/z_a e)\ln(C/C_0)\ , \tag{49}$$

where C is given by Eq. (48), and the size of the space charge is given by the matching condition $-x_I^3 J=(3\delta U/2)^2\epsilon\epsilon_0\mu_c/2$, because one expects a potential drop of order δU across the charged layer. [Let us recall that this last matching condition comes from the integration of the Poisson equation across the charged layer; this integration is not modified by the convective motion, because the convective motion is supposed to be constant throughout the cell, see Eqs. (19)–(25) of this paper and Eqs. (23)–(26) of Ref. [16].] x_I then is

$$x_I=\left[\frac{9\mu_c\delta U^2\epsilon\epsilon_0}{-8eC_0[v+(\mu_c+\mu_a)E_0]}\right]^{1/3}\ . \tag{50}$$

As we see, the variation of the space charge is very simple. One has to replace the recession speed of the anions by the sum of the advective term plus the recession speed of the anions. The main conclusion remains that the size of the space charge decreases with the fluid flow when the fluid flow is incoming in the active zone. The expansion of x_I for slow fluid speeds gives simply

$$x_I=x_I^0[1-v/3(\mu_c+\mu_a)E_0]\ . \tag{51}$$

Roughly, one obtains this result from the equilibrium case without growth by replacing (kT/zeL) by E_0. kT/zeL ($\sim$0.025 V/cm) is the field which is found across the cell in the case without growth (Sec. II of this paper and Sec. II of Ref. [16]; this field is very small because the main part of the potential drop is found across the charged layer). E_0 is the field which is imposed in the bulk ($\sim$10 V/cm) in the case of growth of a flat uniform sheet, ahead of the deposit (see also Sec. III B of Ref. [16], and especially Fig. 5, p. 7362).

The simple derivation of the size of the space charge as a function of the speed of the incoming fluid, which we propose in this section, may be particularly relevant in the case of growth of very compact deposits and especially in the case of growth of needle dendrites, which look often like flat feathers, with a sharp edge (though not straight). However, it does not apply, without further care, to the dense branching regime of electrodeposits, or to the ramified ("fractal") regime, because the fluid flow is not laminar in these instances, as it is already known [18,19,22,24]. We now turn to this more difficult case.

B. Case of a two-dimensional comb

We will not attempt to address the full case of growth of a usual ramified deposit, which will be shown below to be very complex. However, we shall make a set of simplifications, which allow us to understand qualitatively what happens to the space charge in the active zone when convection is present and to calculate a rough estimate of the size of this space charge.

The deposit will now be considered as an ideal two-dimensional comb. This situation (which is already a drastic simplification of the actual shape of the deposit; see Refs. [10] and [29]) is in fact much more complicated than the cases described in the preceding sections. One could hope of tackling the problem of the growing comb by considering the case of a comb with infinitely small spacing between branches (like in Chazalviel's paper, Sec. III B). Then, analyzing the transport of the ions in the moving frame of the tips would lead to formulas similar to the ones given in the preceding paragraphs. This approach would only be justified if the fluid flow were a laminar fluid flow coming from far away, straight towards the deposit. But the actual situation is not like this. The problem stems from the interplay of the Navier-Stokes equation with the boundary condition (a growing deposit). The set of equations which must be solved is

$$\frac{\partial C_c}{\partial t}=D_c\Delta C_c-\mu_C\mathbf{E}\cdot\nabla C_c-\mu_c C_c\,\mathrm{div}\mathbf{E}-\mathbf{v}\cdot\nabla C_c\ , \tag{52}$$

$$\frac{\partial C_a}{\partial t}=D_A\Delta C_a+\mu_a\mathbf{E}\cdot\nabla C_a+\mu_a C_a\,\mathrm{div}\mathbf{E}-\mathbf{v}\cdot\nabla C_a\ , \tag{53}$$

$$\mathrm{div}\mathbf{E}=e(z_c C_c-z_a C_a)/\epsilon\epsilon_0\ , \tag{54}$$

$$\frac{\partial \mathbf{v}}{\partial t}+\mathbf{v}\cdot\nabla\mathbf{v}=\nu\Delta\mathbf{v}-\nabla P+e(z_c C_c-z_a C_a)\mathbf{E}\ . \tag{55}$$

The conservation of the flux which writes $\mathrm{div}\mathbf{v}=0$, become simply $v=\mathrm{const}$ in the one-dimensional cell. However, it is much more subtle in two dimensions and especially around a growing comb (idealized deposit shape). In fact, the fluid flow imposed by the presence of a charge at the tips of the teeth is not laminar. Suppose we consider the deposit as a growing comb, with infinitely thin teeth, which are growing at a constant speed $-\mu_a\mathbf{E}_0$. If we consider the charged zone (which can be expected, in typical conditions, to be very small $\sim 1\ \mu$m) as pointlike, the fluid flow between tips is given [18], in the moving frame, by

$$\psi=v_a x+\frac{s}{24\pi\rho\nu}f\sum_{k=-\infty}^{+\infty}\frac{x-kb}{r_k^2}\ , \tag{56}$$

$$\mathbf{v}=\mathrm{curl}\ \Psi \tag{57}$$

(mind that in these equations x is the coordinate along the comb, while y is the coordinate across the cell; the corresponding y was called x in the former one-dimensional models of Secs. II and III B). b is the distance between branches, s is the thickness of the cell, and f is the total force acting on the fluid at the a given tip. In this model, there are an infinite number of tips, located at abscissa kb, k in $\{-\infty,+\infty\}$.

This shape is of contrarotative vortices between tips and it agrees quantitatively with the observed motion between tips [19]. So assuming a constant fluid flow would simply be wrong. In the moving frame of the tips, the flow is laminar only *far ahead and far behind.* There it has a speed equal to the speed of the moving frame. At the scale of the distance between branches one expects vortices however small the spacing between branches is, in theory. Please note that the difference between the situation described by Eqs. (52)–(57) and the situation described in Sec. II A is not just a matter of mathematical complexity. There is a very important qualitative difference between the flow given by Eqs. (56) and (57) and a constant flow. In the case of a constant flow, there is a global motion of the fluid, with a speed equal to v in the frame of the laboratory, or to make it clearer, *inside the cell.* This means that, in order to achieve experimentally such a situation, one would have to impose a flow across the cell. In the case of the vortices described by Eqs. (56) and (57) there is no global motion of the fluid, the fluid is globally at *rest* in the cell, and it moves *only very near the growing tips,* where it revolves (this is why in Sec. II we considered a growing sheet growing with a speed $-\mu_a\mathbf{E}$ equal to the recession speed of the anions in a convectiveless medium and not with a speed $-\mu_a\mathbf{E}+\mathbf{v}$, which would be the recession speed of the anions in a constant flow). Of course, the conservation of the flux is preserved. A typical shape of the stream near the tips is shown in Fig. 5.

Now the flow given by Eqs. (56) and (57) cannot describe the fluid very close to the tip because the stream function given by Eqs. (56) is singular at the tips $(kb,0)$ (this comes from conservation of the flux: a finite volume of liquid is forced through an infinitely thin funnel). But we know that the space charge *is* very close to the tip. One way of removing the singularities, which was proposed in Refs. [18] and [29] is to introduce a more refined fluid flow whose stream function is the analog of the one given in Eq. (56), after replacing the $(x-kb)/r^2$ functions by $(1/4a)\ln(r_{ka}/r_{-ka})$, where r_{ka} is the distance to a vortex centered at $(kb+a,0)$ and r_{-ka} is the distance to a symmetrical vortex centered at $(kb-a,0)$. By doing so, the tip, which was formerly supposed to be infinitely thin, is now replaced by a tip of width $2a$ (the width a is much smaller than the distance between branches: $2a<b$). One still finds two symmetrical vortices on each side of the tips, but the distance between the centers of these vortices is no longer zero but $2a$. The distance between the branches is still b. Please note that one recovers the previous Eq. (56) by letting a go to zero in the new

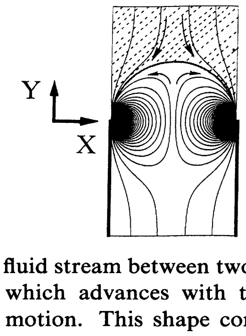

FIG. 5. The fluid stream between two neighboring tips, in the moving frame which advances with the anions. The arrows show the fluid motion. This shape compares rather well with the observed one, except in the zone of the tip, where this theoretical stream is singular, while the real stream, of course, is not. The dashed area is the concentrated area, where the concentration is almost constant, and equal to the bulk concentration. Inside the vortices, the concentration is almost equal to zero. Hence the cations go towards the tip through some kind of a funnel which lies above the vortices (the dashed zone).

stream function:

$$\psi = v_a x + \frac{s}{96a\pi\rho\nu} f \sum_{k=-\infty}^{\infty} \ln \frac{r_{ka}}{r_{-ka}} . \tag{58}$$

Of course, this model is satisfactory only in that it allows a finite size of the funnel at the tip and a finite velocity of the incoming fluid, and because the limit of this model for small thickness (small a) is the singular model, which is known to describe the observed situation very accurately at a reasonable distance from the tip. However, we acknowledge that the real stream function, close to the tip, is certainly more complicated than the one given by Eq. (58).

Without even considering the entire complexity of the interplay of drift, diffusion, and convection very close to the tip of the growing bunch of dendrites, one understands that it is not easy to extend the calculations of Sec. II A to the two-dimensional case. One needs to remove the approximation of a pointlike space charge, then integrate fully the set of equations Eqs. (52)–(55), in order to find the exact shape of the fluid flow, of which Eqs. (56) and (58) are mere approximations. A very refined calculation, or, more likely, a numerical calculation, seems to be required. In view of all the other approximations (convective flow, almost two-dimensional flow, ideal comb, constant chemical parameters, etc.) we will not aim here at such a level of accuracy and will propose the following simple discussion. This discussion relies on the known shape of the concentration maps and on the approximation of the fluid flow given by Eq. (58). It is known experimentally that in many instances, especially when the vortices are in stationary state (for example, with copper sulphate 10^{-2} mol l^{-1} in a cell 1 cm×1 cm and 0.1 mm thick, and a potential difference of about 10 V—see Fig. 6 and Refs. [18,19,30]), the fluid pattern shows the convective vortices on each side of the tips and these vortices are quantitatively described by the ones described by Eq. (58). The two vortices merge at the tip, where they make some sort of a funnel. This funnel is rather thin (small a) and the fluid speed ahead of the tip at a point $(0,y)$ [the tip being at (0,0) in the moving frame] is given, with our assumptions, by $\partial_x \Psi$ at $x=0,y$. This is roughly

$$v_y \sim -[sf/12a\pi\rho\nu(a^2+y^2)]+v_a , \tag{59}$$

if we neglect the effect on the "tip" at coordinate (0,0) of the other "tips." As we see, the incoming velocity of the fluid is not a constant in the vicinity of the tip. It is reasonable to make the approximation that the fluid speed is of the shape given by Eq. (59), somewhere outside the charged layer, not too far ahead of the tip, because the size of the space charge is really very small. Concerning the concentration maps, it is already known that the concentration map induced by these vortices is shaped like a funnel [18,19]. Moreover, the anions are frozen in the moving frame, their concentration is almost constant in the funnel and equal to the bulk concentration "far" ahead, and so is the concentration of cations [18,19]. The fact that the anions are frozen implies that the drift velocity is equal in magnitude and opposite in direction to the fluid speed (neglecting the diffusion term in the funnel), so we know the magnitude of the field "far" ahead of the branch, in the funnel, in the region where we take Eq. (59) as the shape for the fluid field. What we are interested in is the shape of the charged layer which is found "very close" to the tip itself.

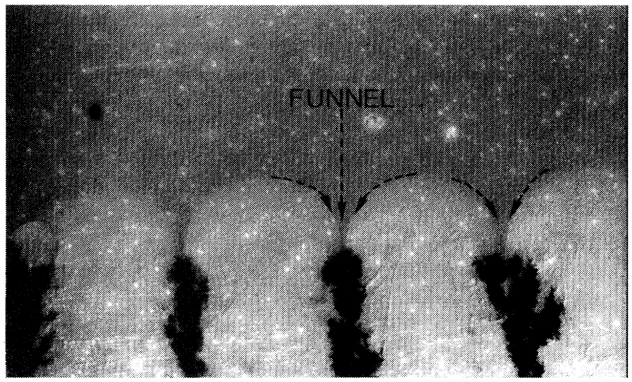

FIG. 6. Experimental observation of the fluid motion, in typical conditions (cell dimensions 1 cm ×1 cm ×0.1 mm, copper sulphate, concentration 5×10^{-2} mol l^{-1}, voltage 5 V). The fluid motion is made visible by means of small droplets of oil (hence the rough aspect of the picture). The oil droplets are trapped in the deposit and do not penetrate inside the vortices, hence the upper part of the picture appears darker than the inner part of the vortices; this allows us to see the funnel which is formed on top of the contrarotative vortices, which are found on each side of a tip. The concentration of copper sulphate is almost constant in this funnel. The space charge is found at the foot of the arch, in a very narrow region, which probably encompasses a small part of the branch. The fluid flow, which is always inwards at the tips, reduces the size of the space charge by a factor $\approx 1.2(E_{\text{bulk}}/v)^{1/3}$, where v is the speed at the tip.

Very close to the tip, the funnel is very straight and the concentrated zone is like a long thread whose thickness is the thickness of the funnel. Then, if we want to compute a very approximate distribution of charges near the tip, we can forget the complexity of the fluid flow and the field at the larger scale of the distance between branches and rather consider a one-dimensional problem in which a single tooth of width $2a$ faces a concentrated zone of width $2a$ in which the fluid speed, instead of being a constant, is given far away by the previous function [Eq. (59)]. In the preceding sentences, "far away" means at a distance $L \gg X_I$, where X_I is the thickness of the charged layer.

We are then back to a problem which is very similar to the one treated in Sec. II B: a tooth grows with a speed $v_a = -\mu_a \mathbf{E}_0$ (where $\mathbf{E}_0$ is the field in the bulk). There is an incoming fluid flow whose velocity varies according to Eq. (59), so the fluid speed and the electric field on some arbitrary boundary at a distance L will be given by $E(L)=v(L)/\mu_a$, with $v(L)$ given by Eq. (59). Also, the concentrations are equal to the bulk concentrations on this boundary. With this simple picture in mind, one understands the effect of convection on the space charge. As in the case discussed in Secs. II A and III A, the effect of the fluid motion is to reduce the size of the charged layer. Apart from some numerical factors, the new space-charge region will be given approximately by a relation analog to Eq. (50), in which one has to put a very large fluid speed and a very large electric field, which are *a priori* the values just outside the charged layer, at some distance L. Since the charged layer is certainly very small ($\sim 1\ \mu$m), one can take the speed which is observed at the tip. The field is simply v/μ_a, because the anions are frozen.

Of course, this model is only qualitative, because it makes use of a one-dimensional approximation of a two-dimensional problem (not even mentioning all the others approximations). Also, the model does not allow us to calculate the exact value of the fluid speed right at the tip because this depends on the magnitude of the total force at the tip. This total force is the difference between the electroconvective force, which is known, and the viscous drag of the branch, which is now known. It seems a formidable task to calculate even an approximate value of the viscous drag. If the fluid flow were perfectly laminar around and across the tip, one could use an effective hydrodynamical radius equal to the radius of the cross section of the branch. Unfortunately, the fluid flow becomes turbulent inside the branch and such an approximation would be very questionable. However, the electroconvective force alone is an upper limit of the total force acting on the fluid and the qualitative discussion given above shows that it is reduced when convection exists. Actually, if one makes the assumption that the Chazalviel layer is not modified by convection, one finds a huge electroconvective force. Indeed, since the charged layer is depleted of cations, the force density in the charged layer is of the order of $z_c e C_c E$. Because of current conservation the force on the tip is then found to be equal to $(1+\mu_a/\mu_c)eC_0E_0bsx_I$ (a more complete derivation of this is given in Ref. [19]). The numerical value of this force is between two and four orders of magnitude larger than what is required in order to displace the liquid [18] (the viscous drag being ignored). This anomalous value of the force given by Chazalviel's model was one of the initial motivations for the calculation of the space charge as a function of the fluid speed. Though precise measurements have not been performed yet, the experiments show that, right at the tips, the fluid speed (~ 1 mm s^{-1}) is of order a hundred times larger than the growth speed ($\sim 10\ \mu$m s^{-1}): this implies a reduction of the convective force by a factor of order $\sim 4-10$.

IV. DISCUSSION AND CONCLUSION

We have shown in this paper that the electroconvective force at the tip is smaller than what could naively be expected, because the Chazalviel layer is modified by convection. There is a reduction in size of the charge layer, which is roughly given by Eq. (50), as a function of the fluid speed and of the field near the active zone; this is in fact only a function of the fluid speed, because of stationarity of the anions. This may suggest a damping effect of the electroconvective motion, according to the following sequence of events. When the current is switched on, a depleted zone forms near the cathode. Then deposition occurs in this depleted zone. Meanwhile, an electroconvective motion sets in. The space-charge region will not become arbitrarily large because, as it tries to increase, it also increases the magnitude of the electroconvective motion. This in turn has a tendency to decrease the size of the space charge, hence the electric force acting on the liquid (note that the viscous drag is increased too). Eventually the space charge reaches an equilibrium value, with a corresponding force and fluid speed. A full two-dimensional calculation is still required in order to calculate the exact shape of the fluid speed in the charged layer. We wish to emphasize that, however, refined the theoretical models may be, the actual deposition on a bunch of dendrites, at the scale of the dendrites ($\leq 5\ \mu$m) is a very complicated three-dimensional problem, in which the fluid flow is certainly turbulent. The model we have presented suggests that the size of the space charge, in the active zone, is limited by hydrodynamical effects. This may also suggest an explanation for the existence of a limiting value of the potential drop which is found at the tips during growth and for the variations of this potential drop in the first stages of growth, when hydrodynamical effects set in [29,30]. Also, variations of the potential drop and the hydrodynamical flow, and hence of the morphology of the deposit, may occur when the acidic front coming from the anode meets the tips of the deposit (the so-called Hecker effect) [31,32].

In ordinary circumstances, the question remains of how the limiting value of the fluid speed depends on the field facing a given branch. This point is of crucial importance for the study of the morphology as a function of the electric field in the bulk, because the typical distance between branches is *ipso facto* equal to twice the typical size of an eddy, and the typical size of an eddy is determined by the force at the tip. We have proved in this paper that this force depends on the fluid speed.

Also, one can wonder whether the fluid motion at the tip may provide a stabilizing mechanism for the growth. As a matter of fact, in the model presented in Sec. III, the growth speed of a given branch is given by the field in the bulk and there is no way of introducing a modification of this growth speed by the fluid flow. However, it may be possible that the deposition mechanism itself depends in some way on fluid flow in the vicinity of the tips; this in turn could give rise to variations of the growth speed [33,34].

Generally speaking, one should expect the convective motion to attenuate the growth of dendrites. The effect of the convective motion is to reduce the existing space charge an electric field in the active zone. Therefore, the instability which gives rise to the growth is attenuated, and hence the process of ramified growth is hindered. One should expect growth of dendrites to be more difficult, or even impossible, in a very fast incoming stream of fluid. Indeed, attempts to grow dendrites in a laminar stream facing the deposit gave very small growth speeds. However, the stream would very soon break the trees, and the experiments could not be carried out in a quantitative way.

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[33] The problems of the stability of the envelope and the origin of the dense radial or dense parallel regimes (depending on the geometry of the cell) are considered by many authors as solved by the resistivity mechanism proposed by Grier, Kessler, and Sander [34]. However, Grier, Kessler, and Sander demonstrate that the resistivity mechanism may work in circular geometry, but that it certainly does not work in linear geometry. It seems difficult to believe that a completely different mechanism must be invoked in circular and in parallel geometries. Hence it is highly probable, we believe, that the mechanism they propose does not work in circular geometry either. In view of the complexity of the fluid motion in the vicinity of the tips, which has been theoretically and experimentally demonstrated, it seems sensible to investigate the role of the fluid motion on the geometry of the deposit. In particular, it seems, from careful scrutiny of the growths, that the fluid flow is so fast at the tip that the copper has virtually not enough time to deposit on the outwards of a tip. As a consequence, it deposits across a rather deep zone, all the deeper as the fluid flow is faster. This effect has a profound effect on the structure of the active zone, which, in our opinion, deserves further investigation.

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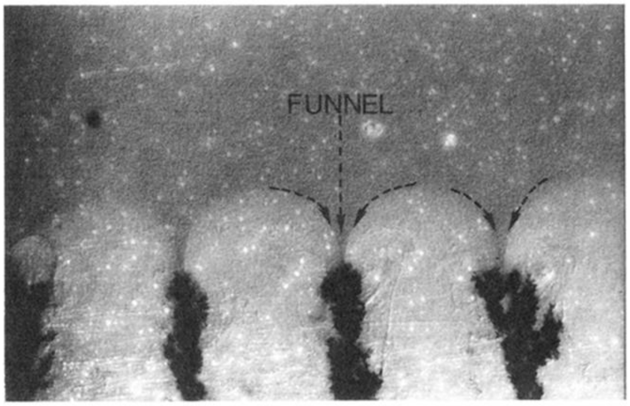

FIG. 6. Experimental observation of the fluid motion, in typical conditions (cell dimensions 1 cm × 1 cm × 0.1 mm, copper sulphate, concentration 5×10^{-2} mol l^{-1}, voltage 5 V). The fluid motion is made visible by means of small droplets of oil (hence the rough aspect of the picture). The oil droplets are trapped in the deposit and do not penetrate inside the vortices, hence the upper part of the picture appears darker than the inner part of the vortices; this allows us to see the funnel which is formed on top of the contrarotative vortices, which are found on each side of a tip. The concentration of copper sulphate is almost constant in this funnel. The space charge is found at the foot of the arch, in a very narrow region, which probably encompasses a small part of the branch. The fluid flow, which is always inwards at the tips, reduces the size of the space charge by a factor $\approx 1.2(E_{\text{bulk}}/v)^{1/3}$, where v is the speed at the tip.