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Asymptotic current-voltage relations for currents exceeding the diffusion limit

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We consider the one-dimensional transport of ions into a perm-selective solid. Direct attempts to evaluate the current-voltage characteristics for currents exceeding the diffusion limit are frustrated by the appearance of nonconverging integrals. We describe how to overcome this obstacle using a regularization scheme.

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I. INTRODUCTION

Understanding the passage of ionic currents through ion-selective solids (e.g., membranes, reactive electrodes, and permeable granules) is a fundamental problem of classical physics with applications to electrodialysis [1,2], nanodevices [3–6], thin-film batteries [7], and ionic channels [8]. Similar transport processes occur in solid electrolytes [9,10] and semiconductors [11,12].

A typical scenario entails one-dimensional (1D) transport through an ideal ion-selective membrane. While classical analysis predicts a diffusion-limited current saturation [13], both experiments and numerical analyses [14,15] have shown the possibility of “overlimiting” currents, which exceed the diffusion limit. The physical mechanism which allows such currents was explained by Rubinstein and his colleagues using singular-perturbation methods [1,2,16] and the transformation from underlimiting to overlimiting currents was explained in detail by Zaltzman and Rubinstein [17]. The inherent instability of overlimiting currents [1,2,5,6,16,18,19], together with the recent discovery of second-kind electro-osmosis at overlimiting conditions [20–22] and the consequent applications to nonlinear electrophoresis of semipermeable granules [23–27], further emphasizes the necessity to understand the basic 1D transport process.

A fundamental problem in that context is the calculation of the current-voltage ($j-V$) relation. This relation is well known for underlimiting currents, whereby j saturates exponentially at large V [see Eq. (28)]. For currents exceeding the diffusion limit, however, this calculation is obstructed by the appearance of nonconverging integrals (see [28]). It is the goal of this paper to present an asymptotic derivation of the $j-V$ characteristics for overlimiting currents using a systematic regularization procedure.

Toward this end, we will consider the simplest 1D configuration [1,2,24] of an electrolyte solution, which is bounded between an anion-impermeable planar membrane and a well-stirred Ohmic bulk. While our scheme can be generalized to more realistic systems [16,17,28], we prefer to demonstrate it for the *simplest* electrochemical cell that exhibits all the essential characteristics of the 1D transport mechanism.

II. PROBLEM FORMULATION

Following [2,24], the idealized configuration we consider comprises a symmetric electrolyte solution (permittivity ϵ, ionic diffusivities $D^{\pm}$, and valencies $\pm\mathcal{Z}$), which is in contact with an ideal cation-selective membrane, impermeable to anions. As in [2,24] we assume that at distance L from the membrane the electrolyte interfaces a well-stirred Ohmic bulk characterized by an identical molar concentration, say c_{∞}, of both ionic species.

We employ the dimensionless notation of [2]; thus, the coordinate x (normal to the membrane), the molar concentrations $c^{\pm}$, and electric potential φ are, respectively, obtained by normalizing with L, c_{∞}, and $RT/\mathcal{Z}\mathcal{F}$ (R being the gas constant, T the absolute temperature, and $\mathcal{F}$ the Faraday constant—a mole of charge). The membrane ($x=0$) is maintained at a negative electric potential, say $-V$, relative to the bulk ($x=1$). Our interest lies in the steady-state transport, and specifically in the electric current in the system as a function of V. When seeking a one-dimensional solution, ionic conservation at steady-state conditions implies that the cations experience a uniform flux (normalized with $D^{+}c_{\infty}/L$), say $2j$, directed toward the membrane. Integration of the appropriate Nerst-Planck equation then reads

$$\frac{dc^{+}}{dx}+c^{+}\frac{d\varphi}{dx}=2j. \tag{1}$$

The membrane impermeability to anions, on the other hand, necessitates zero anionic current,

$$\frac{dc^{-}}{dx}-c^{-}\frac{d\varphi}{dx}=0. \tag{2}$$

The electric current toward the membrane, normalized with $\mathcal{Z}\mathcal{F}D^{+}c_{\infty}/L$, is therefore $2j$. Note that Eq. (2) implies a Boltzmann distribution for c^{-}; with no loss of generality we take $\varphi=0$ at $x=1$, whence

$$c^{-}=e^{\varphi}. \tag{3}$$

The ionic transport is coupled to the electric potential, itself governed by the Poisson equation

$$\frac{d^{2}\varphi}{dx^{2}}=-\frac{c^{+}-c^{-}}{2\delta^{2}}. \tag{4}$$

Here, $\delta=\lambda/L$ in which λ is the Debye thickness,

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$$\lambda^2 = \frac{\epsilon RT}{2\mathcal{Z}^2\mathcal{F}^2 c_\infty}. \tag{5}$$

It is useful to define the charge density (normalized with $2\mathcal{Z}\mathcal{F}c_\infty$), q, and the average ("salt") concentration (normalized with c_∞), c,

$$q = \frac{c^+ - c^-}{2}, \quad c = \frac{c^+ + c^-}{2}. \tag{6}$$

These two variables can be used instead of $c^\pm$. Moreover, it is convenient to employ the electric field

$$E = -\frac{d\varphi}{dx} \tag{7}$$

instead of φ. Thus, addition of Eqs. (1) and (2) yields the salt balance

$$\frac{dc}{dx} - qE = j, \tag{8}$$

while subtraction of these equations yields the charge balance

$$\frac{dq}{dx} - cE = j. \tag{9}$$

The Poisson Eq. (4), moreover, adopts the form

$$q = \delta^2\frac{dE}{dx}. \tag{10}$$

The preceding differential equations are supplemented by appropriate boundary conditions. Being ideal, the membrane at $x=0$ is imposing a fixed cation concentration, say p,

$$x = 0: \quad c^+ = p. \tag{11}$$

At $x=1$, on the other hand, the requirement of interfacing the Ohmic region implies

$$x = 1: \quad c^\pm = 1. \tag{12}$$

In principle, another boundary condition is required to uniquely specify the problem and determine j: this is the imposed-voltage condition $\varphi(x=0)=-V$. Here, following the standard approach [2,15,24], we conveniently replace the potentiostatic problem by an equivalent galvanostatic problem, assuming j prescribed and calculating V.

The preceding equations constitute a well-posed problem for all δ values. As shown by Rubinstein [29], these equations can be captured by a single master equation: substitution of Eq. (10) into Eq. (8) followed by integration yields, upon making use of Eq. (12),

$$c = j(x - x_*) + \frac{1}{2}\delta^2[E^2 - E^2(x=1)], \tag{13}$$

wherein

$$x_* = 1 - \frac{1}{j}. \tag{14}$$

A similar master equation was obtained by Ben and Chang [24]. Substitution of Eqs. (10) and (13) into Eq. (9) then yields a single equation for E (see also [15]),

$$\delta^2\left[\frac{d^2E}{dx^2} - \frac{1}{2}E^3 + \frac{1}{2}E^2(x=1)E\right] - Ej(x - x_*) = j. \tag{15}$$

III. THIN DEBYE LAYER LIMIT

A. Electroneutral region

In virtually all realistic scenarios the Debye thickness is small, $\delta \ll 1$. Because of the appearance of δ^2 as a multiplicative factor in the highest-order derivative of Eq. (10), that asymptotic limit is a singular one. This singularity is reflected in the presence of a boundary layer (the Debye layer) of width $O(\delta)$ about $x=0$. Accordingly, we define the "outer" coordinate X, which is appropriate to describe all processes occurring outside that layer. Thus, in contrast to the membrane-electrolyte interface $x=0$, the value $X=0$ corresponds to the outer edge of the Debye layer.

Asymptotic solutions for all variables as a function of X are then sought via the generic regular expansion in δ,

$$f(X;\delta) \sim f_0(X) + \delta f_1(X) + \delta^2 f_2(X) + \cdots. \tag{16}$$

Poisson's Eq. (10) implies leading-order electroneutrality, $q_0(X)=0$, whereby $c_0^\pm(X)=c_0(X)$. Then, both the salt balance (8) and (16) yield a linear salt profile for both ionic species,

$$c_0 = j(X - x_*). \tag{17}$$

The leading-order electric field is provided by Eq. (9),

$$E_0 = -\frac{1}{X - x_*}. \tag{18}$$

The electroneutral solution is also obtainable from the master Eq. (15), which clearly possesses an asymptotic expansion of the form of Eq. (16),

$$E \sim E_0 + \delta E_1 + \delta^2 E_2 + \cdots \tag{19}$$

in which E_0 is given by Eq. (18). Noting that $E(x=1) \sim -j + o(1)$ readily leads the way to a recursive solution of Eq. (15), where $E_1=0$ and

$$E_2 = -\frac{3}{2j(X - x_*)^4} - \frac{j}{2(X - x_*)^2}. \tag{20}$$

In view of Eqs. (18) and (20), it is evident that the expansion (19) is asymptotic provided $X - x_* \gg \delta^{2/3}$. If in addition $X - x_* \ll 1$ the first term in Eq. (20) dominates its successor.

B. Cathodic Debye layer

In general, the linear cation profile (17) does not satisfy the cathodic condition (11), and an electrically charged cathodic boundary layer (CBL) of width δ is established near $x=0$, wherein the leading-order ionic concentrations differ. The Debye-layer structure is universal, independent to leading order upon the macroscale geometry. Indeed, because of the scale disparity the ionic current does not affect the leading-order layer structure, whereby the Nerst-Planck integrals (1) and (2) readily yield the Boltzmann distributions,

$$c_0^{\pm}(\bar{x}) = c_0(X=0)\exp\{\mp[\varphi_0(\bar{x}) - \varphi_0(X=0)]\}. \tag{21}$$

Here,

$$\bar{x} = x/\delta \tag{22}$$

is a re-scaled Debye-layer coordinate, and $c_0(X=0)$ [$=1-j$, see Eqs. (14) and (17)] is the ionic concentration just outside the Debye layer, corresponding to $\bar{x}\to\infty$. Substitution of Eq. (21) into Eq. (10) yields the Poisson-Boltzmann equation for the Debye-layer electric field,

$$\frac{d^2\varphi_0}{d\bar{x}^2} = (1-j)\sinh[\varphi_0(\bar{x}) - \varphi_0(X=0)]. \tag{23}$$

The Gouy-Chapman solution of this equation, corresponding to an $O(1/\delta)$ electric field, is well known [2]; at large $\bar{x}$, the electric potential decays exponentially fast to the electroneutral value $\varphi_0(X=0)$. An important quantity in that solution is the total Debye-layer voltage (the "zeta potential"), which is given to leading order by

$$\zeta_0 = \varphi_0(\bar{x}=0) - \varphi_0(X=0). \tag{24}$$

The evaluation of ζ_0 does not require the detailed Gouy-Chapman solution; rather, application of Eq. (11) in conjunction with Eq. (21) yields

$$\zeta_0 = \ln(1-j) - \ln p. \tag{25}$$

C. Cell voltage

The cell voltage V is obtained from electric field integration across the cell. The large-$\bar{x}$ exponential decay of the Gouy-Chapman distribution allows writing the leading-order voltage as the sum

$$\int_0^\infty \frac{d\varphi_0}{d\bar{x}}d\bar{x} + \int_0^1 \frac{d\varphi_0}{dX}dX = -\zeta_0 - \int_0^1 E_0(X)\,dX. \tag{26}$$

The electroneutral voltage is obtained from Eqs. (14) and (18),

$$\int_0^1 E_0(X)\,dX = \ln(1-j). \tag{27}$$

Substitution of Eqs. (25) and (27) into Eq. (26) yields the familiar $j-V$ correlation [13],

$$V \sim \ln\frac{p}{(1-j)^2}. \tag{28}$$

IV. OVERLIMITING RÉGIME

A. Diffusion layer and space-charge layer

The approximation (28) clearly implies the upper limit $j=1$, which corresponds to a saturated diffusive current, whereby c_0 vanishes near the cathode [see Eq. (17)]. It is well known however from both experiments and numerical simulations [14] that overlimiting currents ($j>1$) appear at sufficiently large voltages. It was indeed shown by Rubinstein and his colleagues [14,30] that for $O(\ln\delta)$ voltages the preceding asymptotic expansions break down, and that for $O(1/\delta)$ large voltages a new overlimiting regime is formed where $j-1=O(1)$.

The possibility of an overlimiting current has to do with the nonlinearity of the system. Consider indeed the master Eq. (15); in addition to the electroneutral expansion (19), it was also shown [2] to possess the expansion

$$E(X,\delta) \sim \delta^{-1}\tilde{E}_{-1}(X) + \tilde{E}_0(X) + \delta\tilde{E}_1(X) + \cdots, \tag{29}$$

corresponding to an $O(\delta^{-1})$ large electric field. Here

$$\tilde{E}_{-1} = -(2j)^{1/2}(x_* - X)^{1/2}, \tag{30}$$

$$\tilde{E}_0 = \frac{-1}{2(x_* - X)}, \tag{31}$$

and

$$\tilde{E}_1 = \frac{5j^{-1/2}}{2^{7/2}(x_* - X)^{5/2}} - \frac{j^{3/2}}{2^{3/2}(x_* - X)^{1/2}}. \tag{32}$$

The series, valid for $X<x_*$, is asymptotic provided $x_*-X \gg \delta^{2/3}$. If, in addition, $x_*-X\ll 1$, the second term in Eq. (32) is negligible compared with the first.

Since the ionic concentrations must be positive, Eq. (17) implies that the original expansion (19) can only hold for $X>x_*$. Thus, while that expansion was valid in the entire cell (except in a thin Debye layer) in the underlimiting case, it only holds at part of the cell in the overlimiting case. The cell is therefore decomposed into two $O(1)$ intervals: a *diffusion layer* (DL) for $X>x_*$ and $X-x_*\gg\delta^{2/3}$, where Eq. (19) holds, and a *space-charge layer* (SCL) layer for $X<x_*$ and $x_*-X\gg\delta^{2/3}$, where Eq. (29) holds. Substitution of Eqs. (29) and (30) into Eq. (13) reveals that the salt concentration is only $O(\delta)$ in the SCL. Moreover, in view of the large $O(\delta^{-1})$ electric field magnitude, the electric potential there transforms from negative $O(1)$ values to negative $O(\delta^{-1})$ values. As a consequence, Eq. (3) implies that the anion concentration there becomes exponentially small. Since $c-q=c^-$, it follows that the SCL is quantified by $O(\delta)$ charge density (this can also be seen from Poisson's equation), as opposed to the $O(\delta^2)$ charge density in the DL.

To illustrate the difference between the underlimiting and overlimiting regimes, and, specifically, the unique characteristics of the DL and SCL at the latter, we numerically solved the galvanostatic boundary-value problem (8)–(12) for $\delta=0.01$ and $p=2$ (using a standard shooting method). The resulting ionic concentration profiles are shown in Fig. 1 for the underlimiting-current case $j=1/2$ and for the overlimiting-current case $j=2$ (where $x_*=1/2$), the latter clearly illustrating the DL-SCL decomposition. This decomposition is also shown in Fig. 2, where the numerically calculated electric field (for $j>1$) is compared with the appropriate approximations in both the DL and SCL regions.

B. Transition layer

As explained by Rubinstein and Zaltzman [2], the DL and SCL are connected by an $O(\delta^{2/3})$-wide transition layer (TL)

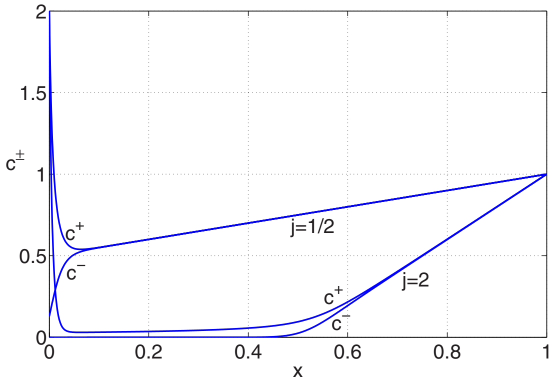

FIG. 1. (Color online) Ionic concentrations for δ=0.01 and p=2 for both underlimiting (j=1/2) and overlimiting (j=2) currents, obtained using numerical solution of the boundary-value galvanostatic problem (8)–(12).

about x_*. This layer is naturally analyzed using the transformation

$$x - x_* = j^{-1/3}\delta^{2/3}z, \quad E = j^{1/3}\delta^{-2/3}F, \tag{33}$$

which transforms the master Eq. (15) into

$$\frac{d^2F}{dz^2} = \frac{1}{2}F^3 + zF + 1 - \frac{\delta^{4/3}}{2j^{2/3}}E^2(x=1)F. \tag{34}$$

At large z, this equation possesses the expansion [cf. Eqs. (18)–(20)]

$$F \sim -\frac{1}{z} - \frac{3}{2z^4} + \cdots, \tag{35}$$

while as $z \to -\infty$ [cf. Eqs. (29)–(32)],

$$F \sim -(-2z)^{1/2} + \frac{1}{2z} + \frac{5}{2^{7/2}(-z)^{5/2}} + \cdots. \tag{36}$$

These approximations are obtained by neglecting the last term in Eq. (34) and are therefore valid provided the limit $z \gg 1$ is modified to $1 \ll z \ll \delta^{-2/3}$. Thus, to leading order, F is a universal function, independent of both δ and j.

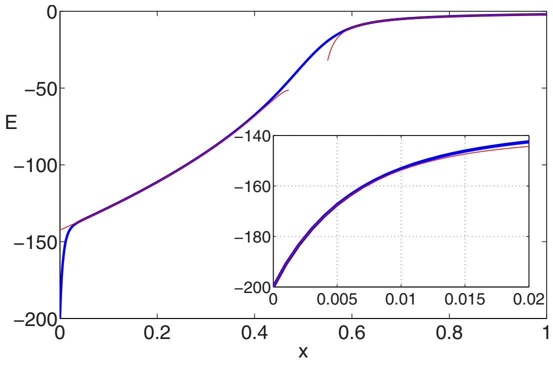

FIG. 2. (Color online) The electric field distribution for δ=0.01, p=2, and j=2. The thick line depicts the numerical solution of the boundary-value problem (8)–(12). The thin lines represent the DL expansion (19) and SCL expansion (29). The inset zooms on the near-membrane region, the thin line representing the CDL approximation $\delta^{-1}E_{-1}(\bar{x})$ [see Eq. (38)].

C. Anion-free cathodic boundary layer

As in the case of underlimiting currents, the outer solution near x=0 fails to satisfy the boundary condition (11), and a CBL is again established about x=0. This layer is again characterized by $O(\delta)$ thickness and is therefore described by the Debye-scale variable $\bar{x}$ [see Eq. (22)]. However, it now needs to match the SCL outer solution rather then the electroneutral solution. The need to match about an $O(\delta^{-1})$ strong electric field and an exponentially small anion concentration implies a structure which differs fundamentally from the Gouy-Chapman one [see Eq. (21)]. This new structure was resolved by Chu and Bazant [28] who postulated, as in the underlimiting-current case, that the electric field is $O(1/\delta)$ and the cation concentration is $O(1)$,

$$E \sim \delta^{-1}E_{-1}(\bar{x}) + \cdots, \quad c^+ \sim c_0^+(\bar{x}) + \cdots, \tag{37}$$

but that the anion concentration is exponentially small. Solving the Debye-scale equations then yields [28]

$$E_{-1} = -2m\coth(m\bar{x} + n), \tag{38a}$$

$$c_0^+ = \frac{4m^2}{\sinh^2(m\bar{x} + n)} \quad (n > 0). \tag{38b}$$

Asymptotic matching to the SCL solution yields here $m = \sqrt{jx_*/2}$; condition (11) then yields $\sinh n = \sqrt{2jx_*/p}$.

V. VOLTAGE CALCULATION IN THE OVERLIMITING RÉGIME

A. General scheme

While the voltage is $O(1)$ in the underlimiting-current régime [see Eq. (28)], it becomes $O(\delta^{-1})$ for overlimiting currents, wherein the leading-order voltage is contributed by the SCL [see Eqs. (29) and (30)],

$$V \sim -\delta^{-1}\int_0^{x_*}\tilde{E}_{-1}(X)\,dX = \frac{2^{3/2}j^{1/2}x_*^{3/2}}{3\delta}. \tag{39}$$

For many applications, it is desired to obtain a systematic asymptotic approximation for V in the limit $\delta \to 0$, up to $O(1)$ terms. Exploiting the integrable structure of the semibounded geometry, Ben and Chang [24] showed that the voltage can be calculated once the electric field is evaluated on the cathode. Thus, using matched asymptotic expansions, these authors improved the estimation (39), thereby clarifying the asymptotic structure of the j-V relation.

Our approach is distinct from that of Ben and Chang [24]: we calculate the voltage directly by integrating the electric field across the cell. While this robust scheme is applied here for the idealized semibounded geometry (with the objective of emphasizing the asymptotic scheme), it is easily generalized to more realistic electrochemical cell models. Our goal here is to calculate the voltage approximation up to $O(1)$ accuracy, thereby complementing the underlimiting-current formula (28). Unlike the underlimiting-current case, however, the voltage calculation cannot be carried out by simple summation of the respective contributions from the various asymptotic regions (four of them now), since these contributions appear as nonconverging integrals. We here show how to address this obstacle using a regularization method. The voltage is decomposed into four contributions

$$V=\left(\int_0^{\eta}+\int_{\eta}^{x_*-\xi}+\int_{x_*-\xi}^{x_*+\xi}+\int_{x_*+\xi}^{1}\right)\frac{d\varphi}{dx}dx. \tag{40}$$

The auxiliary parameters η and ξ are at our disposal; without loss of generality they are assumed $\ll 1$, whereby the four contributions are conceptually associated with the CBL, SCL, TL, and DL, respectively. We further assume $\delta \ll \eta(\ll 1)$ and $\delta^{2/3} \ll \xi(\ll 1)$. Our goal is to calculate the four contributions up to $O(1)$. While these contributions may depend upon η and ξ, their sum must be independent of these arbitrary parameters.

The CBL and DL contributions are obtained using Eqs. (18) and (38), respectively,

$$\int_0^{\eta}\frac{d\varphi}{dx}dx=-\delta\int_0^{\eta/\delta}E(\bar{x})\,d\bar{x}\sim(2jx_*)^{1/2}\frac{\eta}{\delta}+2n-3\ln 2-\ln\frac{jx_*}{p}+o(1), \tag{41}$$

$$\int_{x_*+\xi}^{1}\frac{d\varphi}{dx}dx\sim\ln(1-x_*)-\ln\xi+o(1). \tag{42}$$

The first term in Eq. (41) diverges with $\eta/\delta(\gg 1)$; it is associated with the CBL structure at overlimiting currents, wherein the leading-order electric field (38a) approaches a large uniform value as $\bar{x}\to\infty$ (as opposed to the comparable exponential decay in the underlining-current case). The second term in Eq. (42), which originates in the $1/x$-type behavior of the DL electric field (18) in the vicinity of x_*, diverges as well.

The contribution of the SCL is obtained using the expansion (29),

$$\int_{\eta}^{x_*-\xi}\frac{d\varphi}{dx}dx\sim-\delta^{-1}\int_{\eta}^{x_*-\xi}\tilde{E}_{-1}(X)\,dX-\int_{\eta}^{x_*-\xi}\tilde{E}_0(X)\,dX+o(1). \tag{43}$$

To the same order of approximation, it is legitimate to replace η by 0 in the second integral (but not in the first). Substitution of Eqs. (30) and (31) and using the binomial expansion yields here

$$\int_{\eta}^{x_*-\xi}\frac{d\varphi}{dx}dx\sim\frac{2^{3/2}j^{1/2}}{3\delta}(x_*^{3/2}-\xi^{3/2})-(2jx_*)^{1/2}\frac{\eta}{\delta}+\frac{1}{2}\ln\frac{x_*}{\xi}+o(1). \tag{44}$$

(Obtaining the latter expression necessitates modifying the requirement $\delta\ll\eta\ll 1$ to the stricter one $\delta\ll\eta\ll\delta^{1/2}$.) Thus, the first term in Eq. (41) is canceled by the second term in Eq. (44).

The sum of the preceding three voltage contributions still contains two undetermined terms,

$$-\frac{2^{3/2}j^{1/2}}{3\delta}\xi^{3/2}-\frac{3}{2}\ln\xi, \tag{45}$$

which diverge as $\delta\to 0$ and must therefore be canceled by the TL contribution. Using the transformation (33), this contribution is provided by

$$\int_{x_*-\xi}^{x_*+\xi}\frac{d\varphi}{dx}dx=-\int_{-j^{1/3}\xi/\delta^{2/3}}^{j^{1/3}\xi/\delta^{2/3}}F(z)\,dz. \tag{46}$$

Even when interest lies only in leading-order term, evaluating this integral requires some caution. While $\xi/\delta^{2/3}\to\infty$, the divergence of the integrand as $z\to-\infty$ [see Eq. (36)] prohibits replacing the upper and lower integration limits with $\pm\infty$. It is therefore necessary to subtract this diverging part. Moreover, even after this is accomplished the integral does not converge in view of the slow $1/z$-type integrand decay for $z\to\pm\infty$ [see Eqs. (35) and (36)]. A naive subtraction of the problematic $1/z$ terms is not helpful here because it results in a nonintegrable singularity at $z=0$. A regularization scheme is therefore required.

B. TL voltage: Regularization method

For $z>0$ and $z<0$ we, respectively, define

$$G(z)=F(z)+\frac{1-e^{-z}}{z},\qquad G(z)=F(z)+(-2z)^{1/2}-\frac{1-e^{z}}{2z}. \tag{47}$$

With these definitions, $G=o(z^{-2})$ for $z\to\pm\infty$ and is integrable over the entire real axis,

$$I=\int_{-\infty}^{\infty}G(z)\,dz\quad\text{exists}. \tag{48}$$

Just like F, G is a universal function at leading order, independent of both δ and j. Accordingly, $I\sim I_0+o(1)$ for small δ, I_0 being a pure number. A straightforward numerical quadrature yields $I_0\doteqdot-0.634$.

In terms of G, the TL voltage contribution (46) is given by

$$\frac{3}{2}\int_0^{j^{1/3}\xi/\delta^{2/3}}\frac{1-e^{-z}}{z}dz+\frac{2^{3/2}j^{1/2}\xi^{3/2}}{3\delta}-\int_{-j^{1/3}\xi/\delta^{2/3}}^{j^{1/3}\xi/\delta^{2/3}}G(z)\,dz. \tag{49}$$

The first integral is evaluated using the asymptotic identity [31]

$$\int_0^{a}\frac{1-e^{-z}}{z}dz\sim\gamma+\ln a+O(e^{-a}/a)\quad\text{as }a\to\infty, \tag{50}$$

wherein γ is Euler's constant. Moreover, the fast $o(z^{-2})$ decay of G at large $|z|$ [see Eqs. (35) and (36)] implies that replacing $j^{1/3}\xi/\delta^{2/3}$ with ∞ in the second integral of Eq. (49) leads to an $o(1)$ error. Thus, we obtain the TL voltage,

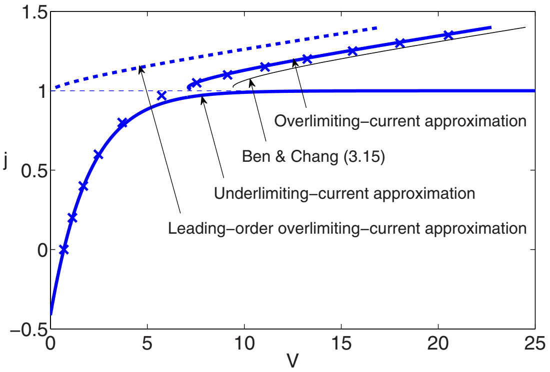

FIG. 3. (Color online) j-V characteristics for $\delta=0.01$ and $p=2$. The crosses denote numerical solution of the boundary-value galvanostatic problem (10)–(12). The solid lines depict the underlimiting-current approximation (28) and the overlimiting-current approximation (52). The dashed curve is the leading-order overlimiting-current approximation (39), and the thin line is Eq. (3.15) of Ben and Chang [24].

$$\frac{3\gamma}{2}+\frac{3}{2}\ln\xi+\frac{1}{2}\ln j-\ln\delta+\frac{2^{3/2}j^{1/2}\xi^{3/2}}{3\delta}-I_0+o(1). \tag{51}$$

Note that Eq. (51) comprises the requisite two inverse terms to Eq. (45).

Adding the contributions (41), (42), (44), and (51) furnishes the j-V approximation, accurate to $O(1)$,

$$V\sim\frac{2\sqrt{2}(j-1)^{3/2}}{3\delta j}+\ln\frac{p}{8\delta j(j-1)^{1/2}}+2n+\frac{3\gamma}{2}-I_0+o(1). \tag{52}$$

As required, this approximation is independent of the artificial parameters η and ξ. In Fig. 3 we compare this approximation to the j-V relation obtained from the numerical solution of the exact problem. This figure also shows how the comparable underlimiting-current approximation (28) matches the numerical calculations for $j<1$.

VI. SUMMARY

We have considered the one-dimensional ionic transport through an electrochemical cell which is bounded by an ideal cathodic ion-selective membrane. A systematic method was constructed for evaluating the j-V relation at overlimiting currents, using a galvanostatic boundary-value formulation. Thus, for any given value of the current j, the transport processes in the cell are calculated by solving a master differential equation in the thin-Debye-layer limit. This highly singular problem is manifested in the appearance of four distinct asymptotic regions. The voltage V is then calculated by integrating the electric field over the cell length. A naive attempt to evaluate it by adding the respective contribution from the four asymptotic domains is frustrated by the appearance of nonconvergent integrals. We here describe how to overcome this obstacle using a careful regularization procedure.

Following previous analyses [1,2,24], and with the objective of illuminating the regularization scheme, we have addressed here an idealized electrochemical model. Idealization is explicit in two aspects: the geometric configuration, which entails only a single-ion-exchange surface ("semibounded" geometry), and the modeling of that surface as an ideal membrane, with a prescribed cationic concentration. While indeed idealized, our model exhibits all the important feature of the overlimiting-current regime.

The present model can be extended without any conceptual difficulty to more realistic electrochemical systems where the artificial "mixed bulk" is replaced with a second ion-exchange surface [15,17] and where the ideal-membrane idealization is replaced with more realistic kinetic models [28]. Because of the need to satisfy an integral constraint (see [15]) in such systems, however, the accompanying analysis is technically involved and therefore tends to obscure the regularization methodology which we want to highlight. Mathematically, the need for regularization arises because of the large-argument behavior of the transition-layer field. Since such a layer is present in virtually all electrochemical processes in the overlimiting regime (see, e.g., [28]), the problem of an indeterminate j-V relation is rather universal.

As a matter of fact, the semibounded model may actually constitute the appropriate local description at the vicinity of curved membranes (e.g., the boundaries of ion-selective granules), whereby its applicability extend beyond the limited class of 1D transport in electrochemical cells. In these problems, wherein the diffusion-layer dimension is set by a global Péclet number, the transport is approximately one dimensional at the vicinity of the granule boundary. When reaching out of that region, the diffusion-layer concentrations approach a uniform mixed-bulk value, as in Eq. (12).

The relevance of the semibounded model to electrophoresis of the second kind is discussed by Ben and Chang [24]. These authors exploit the unique structure of the semibounded geometry to obtain the overlimiting j-V relation using an asymptotic evaluation of the electric field at the membrane surface, thus avoiding the pain of adding the respective contributions from the separate asymptotic domains. The j-V relation (3.15) in [24] coincides with Eq. (52) in both the $O(\delta^{-1})$ leading term and the $O(\ln\delta)$ correction. [Note that both j and δ are defined differently in [24]. Also, there seems to be a typo in the second term of Eq. (3.15) in [24]: the 1/2 exponent should apply to $j-2$.] Using these terms, Ben and Chang [24] obtained a large-flux universal j-V correlation on which a large number of numerical simulations successfully collapsed. In many practical situation it is desirable to go further and obtain a precise expression valid for *moderate* fluxes, as these represent the onset of the overlimiting region. The $O(1)$ terms in relation (3.15) of [24] are only partially similar to those in Eq. (52). The mismatch is observed in Fig. 3.

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