Series solution of Painlevé II in electrodiffusion: conjectured convergence

A J Bracken and L Bass

School of Mathematics and Physics, The University of Queensland, Brisbane 4072, Australia

E-mail: a.bracken@uq.edu.au and lb@maths.uq.edu.au

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Abstract
A perturbation series solution is constructed with the use of Airy functions, for a nonlinear two-point boundary-value problem arising in an established model of steady electrodiffusion in one dimension, with two ionic species carrying equal and opposite charges. The solution includes a formal determination of the associated electric field, which is known to satisfy a form of the Painlevé II differential equation. Comparisons with the numerical solution of the boundary-value problem show excellent agreement following termination of the series after a sufficient number of terms, for a much wider range of values of the parameters in the model than suggested by previously presented analysis, or admitted by previously presented approximation schemes. These surprising results suggest that for a wide variety of cases, a convergent series expansion for the Painlevé transcendent describing the electric field has been obtained. A suitable weighting of error measures for the approximations to the field and its first derivative provides a monotonically decreasing overall measure of the error in a subset of these cases. It is conjectured that the series does converge for this subset.

Keywords: electrodiffusion, Painlevé II equation, series solution, unexpected convergence

(Some figures may appear in colour only in the online journal)

1. Introduction

Theoretical investigations of electrodiffusion—the transport of charged ions in solution—have a long history dating back to the pioneering works of Nernst [1] and Planck [2]. Such processes underpin a variety of important physical and biological phenomena [3–5], including transport of nerve impulses [6–8].
A well-established model in electrodiffusion describes one-dimensional steady transport of two types of ions in solution, carrying equal and opposite charges [9–11]. Charge separation of positive and negatively charged ions arising from differing diffusional fluxes, gives rise to an electric field that acts back on the charges, resulting in nonlinearity of the model and associated mathematical complexity.

Grafov and Chernenko [9] showed that in the special case when only one of the two ionic species has a non-zero flux, across a semi-infinite domain, then a combination of concentration and flux variables satisfies a second-order ordinary differential equation (ODE) that is a form of Painlevé’s second equation PII [12–14]. Independently, one of us [10, 11] showed that in the general case when both fluxes can be non-zero, another form of PII is always satisfied by the variable in the model that describes the electric field, in either a semi-infinite domain or a finite slab modeling a liquid junction. These independent results show possibly the first appearances of PII in applications, more than 50 years ago. In what follows we consider further the case of the slab, specified by two-point boundary conditions (BCs).

A further result obtained in the early studies [10, 11] was an approximate solution and associated asymptotic form for the electric field, appropriate to certain physically well-defined limiting situations in a junction. This result was obtained by linearizing the form of PII satisfied by the field to an inhomogeneous form of Airy’s ODE [15, 16]. In later work, the asymptotic behaviour of the system in other limiting situations was studied using the methods of singular perturbation theory [17–19]. The early results involving PII have also been extended in various other directions [20, 21].

The form of PII found in [10, 11] is quite unusual, with the feature that the coefficients in the ODE depend on the solution itself. This has increased the difficulty of analytical and numerical studies, over and above those that apply to PII in standard form [22, 23]. Nevertheless, existence and uniqueness of solutions has been established [24–26] in situations where physically sensible BCs are imposed on the model. These ‘charge-neutral’ BCs require that, at each face of the slab, the concentration of the positive ions equals that of the negative ions. A wide array of numerical studies has also been carried out [26, 27], and as a result it can safely be concluded that under these BCs the electric field, although described by a Painlevé transcendent, has no singularities in the domain of interest.

Recent research [27–30] has built upon the early results obtained in [10, 11], extending known Bäcklund and Gambier transformations of PII [31–33] to all the variables in the model, and exploring their consequences. One development has been the discovery of the emergent phenomenon of ‘Bäcklund flux quantization’, wherein successive Bäcklund transformations enable the construction of a sequence of exact solutions that reflect the quantization of charge on the ions in solution [34]. Other studies have explored the extension of the model to allow more ionic species in solution, with various valences [35–38]. A particular extension to allow for fixed charges within the junction, together with an arbitrary number of ionic species, has led to new differential equations in the context of electrodiffusion, including a generalization of PII [39].

In what follows we go back to the approach initiated in [10, 11] and, building upon the linearization obtained there as a first approximation, obtain a formal solution of the whole boundary-value problem (BVP) defining the model with charge-neutral BCs, in terms of an infinite perturbation series for the electric field, with each term constructed using Airy functions. The degree of approximation obtained by truncating this series after a chosen number of terms is tested by comparing with the ‘exact’ solution obtained numerically. These comparisons show excellent agreement for a wide range of values of the parameters in the model, going well beyond what is suggested by existing approximations [10, 11, 17]. Most surprising is that, as the number of terms in the series is increased, the degree of approximation achieved suggests
that in these cases the series converges. If this is correct, then in this wide variety of cases the Painlevé transcendent describing the steady electric field is expressed as a convergent series, constructed using Airy functions. It is possible that the series provide asymptotic, rather than convergent approximations but if so, they have a very different character, and a much wider range of applicability, than earlier asymptotic results [10, 11, 17–19]. In any event, we see here a development in which the power of digital computation appears to uncover unexpected possibilities for analytical approaches.

Various connections between PII and Airy’s ODE have been identified and discussed previously [40–42]. In particular there is a well-known sequence of exact solutions of PII expressed in terms of Airy functions and related by Bäcklund transformations [23, 29], and a link between this sequence and the linearization of PII obtained by Bass [10, 11] is known [27] to be provided with the help of the transformation first found by Gambier [31, 33]. Nevertheless, the relationship between solutions of these two ODEs that is suggested by our results, is unexpected in the present context.

Another surprise is the behaviour of the errors in successive approximations to the Painlevé transcendents describing the electric field and its first derivative, especially in cases where the perturbation series appears to converge. These errors typically oscillate in size as they decrease towards zero, and a remarkable relationship between the oscillating errors in the variables describing the field and its derivative is revealed, which can be exploited in some cases to obtain monotonically decreasing error measures. We conjecture that this is a sufficient condition for the series in those cases to converge.

2. The model

The governing system of coupled first-order ODEs for the model is

\[
\begin{align*}
\frac{d \hat{c}_+}{d \hat{x}} &= \left(\frac{ze}{k_B T}\right) \hat{E}(\hat{x}) \hat{c}_+ - \hat{\Phi}_+ / D_+ , \\
\frac{d \hat{c}_-}{d \hat{x}} &= -\left(\frac{ze}{k_B T}\right) \hat{E}(\hat{x}) \hat{c}_- - \hat{\Phi}_- / D_- , \\
\frac{d \hat{E}(\hat{x})}{d \hat{x}} &= \left(4\pi ze / \varepsilon\right) [\hat{c}_+(\hat{x}) - \hat{c}_-(\hat{x})] 
\end{align*}
\]  

(1)

for \(0 < \hat{x} < \delta\). Here \(\hat{E}(\hat{x})\) denotes the electric field within the junction, while \(\hat{c}_+(\hat{x})\) and \(\hat{c}_-(\hat{x})\) denote the number concentrations of the two ionic species; \(\hat{\Phi}_+\) and \(\hat{\Phi}_-\) their steady (constant) number flux-densities in the \(x\)-direction across the junction; \(z\) the common magnitude of their charge numbers; and \(D_+, D_-\) their diffusion coefficients. In addition, \(k_B\) denotes Boltzmann’s constant, \(e\) the elementary charge, \(\varepsilon\) the relative permittivity, and \(T\) the ambient thermodynamic temperature within the solution in the junction.

An important auxiliary quantity is the electric current-density in the \(x\)-direction,

\[
\hat{J} = ze (\hat{\Phi}_+ - \hat{\Phi}_-).
\]  

(2)

As shown in appendix A, after all variables are replaced by dimensionless counterparts, equation (1) take the form

\[
\begin{align*}
\nu E'(x) &= c_+(x) - c_-(x) , \\
\nu E'(x) &= c_+(x) - c_-(x) .
\end{align*}
\]  

for \(0 < x < 1\), with the prime denoting differentiation with respect to \(x\), and (2) becomes
\[ J = \tau_+ \Phi_+ - \tau_- \Phi_- \tag{4} \]

where \( \tau_+ \) and \( \tau_- \) are positive dimensionless constants, to be regarded as known, with
\[ \tau_+ + \tau_- = 1. \tag{5} \]

The positive dimensionless constant \( \nu \) in (3) is defined by (A.2) below, and is also to be regarded as known. It is the squared ratio of an internal ‘Debye length’ to the width \( \delta \) of the junction [10], and it plays an important role in the analysis of the model.

Our concern in the present work is with charge-neutral boundary conditions (BCs) as in (A.1), supplemented by a prescribed value for the current density. In dimensionless form, we have
\[ c_+ (0) = c_- (0) = c_0, \quad c_+ (1) = c_- (1) = c_1 (= 1 - c_0), \quad J = j. \tag{6} \]
where \( c_0 > 0, \) \( c_1 > 0, \) and \( j \) are prescribed constants. Note that the system (3) with BCs (6) admits the ‘reflection symmetry’
\[ c_{R \pm} (x) = c_{\pm} (1 - x), \quad E_R (x) = -E (1 - x), \quad \Phi_{R \pm} = -\Phi_{\pm}, \quad J_R = -J \tag{7} \]
so there is no significant loss of generality caused by our assumption below that \( 0 < c_0 < c_1. \tag{8} \)
(The case \( c_0 = c_1 \) leads to a constant solution that is not of interest in what follows.)

In (3) and (4), \( \Phi_+ \) and \( \Phi_- \) also have constant values, but these values are not prescribed. Rather, they are to be determined, subject to (4) and the last of (6), as part of the solution, together with \( c_+ (x), \) \( c_- (x) \) and \( E (x). \) Thus there are five unknowns, to be determined using the ODEs (3) and the five BCs in (6).

3. Painlevé II boundary-value problem

The BVP defined by (3) and (6) can be rewritten entirely in terms of \( E (x) \) and its derivatives, following [10, 11]. To this end, we note from (3) the first-integral
\[ c_+ (x) + c_- (x) - \frac{1}{2} \nu E (x)^2 + (\Phi_+ + \Phi_-) x = \text{const.}, \tag{9} \]
which gives, on imposing the first two of (6),
\[ c_+ (x) + c_- (x) = \frac{1}{2} \nu E (x)^2 + \left\{ 2(c_1 - c_0) + \frac{1}{2} \nu [E(0)^2 - E(1)^2] \right\} x 
+ 2c_0 - \frac{1}{2} \nu E (0)^2, \tag{10} \]
and
\[ \Phi_+ + \Phi_- = \left\{ 2(c_0 - c_1) + \frac{1}{2} \nu [E(1)^2 - E(0)^2] \right\}. \tag{11} \]
Using the third of (3) and the third of (6), we then have
\[ c_{\pm} (x) = \frac{1}{4} \nu E (x)^2 + \left\{ (c_1 - c_0) + \frac{1}{4} \nu [E(0)^2 - E(1)^2] \right\} x 
+ c_0 - \frac{1}{4} \nu E (0)^2 \pm \frac{1}{2} \nu E'(x). \tag{12} \]
and
\[ \Phi_\pm = \tau \pm \left\{ 2(c_0 - c_1) + \frac{1}{2} \nu [E(1)^2 - E(0)^2] \right\} \pm j, \tag{13} \]
showing that all four of \( c_+(x), c_-(x), \Phi_+ \) and \( \Phi_- \) are determined if \( E(x) \) and \( E'(x) \) can be found for all \( 0 \leq x \leq 1 \).

To find an equation that determines \( E(x) \) and \( E'(x) \), we differentiate the third of (3) once and apply the first two of (3) and (9) to get
\[ \nu E''(x) = \frac{1}{2} \nu E(x)^3 + \left[ 2c_0 - \frac{1}{2} \nu E(0)^2 - (\Phi_+ + \Phi_-) x \right] E(x) - (\Phi_+ - \Phi_-), \]
\[ = \frac{1}{2} \nu E(x)^3 + \left[ 2c_0 - \frac{1}{2} \nu E(0)^2 + \left\{ 2(c_1 - c_0) + \frac{1}{2} \nu [E(0)^2 - E(1)^2] \right\} x \right] E(x) \]
\[ + (\tau_+ - \tau_-) \left\{ 2(c_1 - c_0) + \frac{1}{2} \nu [E(0)^2 - E(1)^2] \right\} - 2j. \tag{14} \]

From the third of (3) and (6), we see that this second-order ODE is to be solved subject to the Neumann BCs
\[ E'(0) = 0 = E'(1). \tag{15} \]
It may be remarked that the derivation given here shows that, in effect, the system of ODEs (3) can be regarded as a Noumi–Yamada system [43, 44] for (14), which has been identified [10, 11] as a form of PII.

This apparent simplification of the BVP, now involving only the single second-order ODE (14), comes at a cost. The coefficients in the ODE involve the unknown values \( E(0) \) and \( E(1) \) which have to be determined as part of its solution. As mentioned above, this complicates the theoretical and numerical analysis [24, 26]. Furthermore, while a suitable scaling of the dependent variable combined with a linear transformation of the independent variable [10, 28],
\[ E(x) = 2\beta y(z), \quad z = \beta x + \gamma, \tag{16} \]
enables (14) to be rewritten in a standard form [12] for PII,
\[ y''(z) = 2y(z)^3 + yz(z) + C, \quad C = \text{const.}, \tag{17} \]
the values of the constants \( \beta \) and \( \gamma \) needed to secure this result, and consequently the value of \( C \), all involve the unknown values \( E(0) \) and \( E(1) \). This limits the usefulness of such a transformation and of the standard form (17) in the present context, and also obscures the interpretation of the results below in terms of solutions of (17).

When the terms quadratic and cubic in the electric field are neglected in (14), the equation is linearized to an inhomogeneous form of Airy’s ODE [15, 16],
\[ \nu E''(x) = \left[ 2c_0 + 2(c_1 - c_0)x \right] E(x) + 2 \left( (\tau_+ - \tau_-)(c_1 - c_0) - j \right). \tag{18} \]
It was the solution of this equation, with the BCs (15), that was used in [10, 11] to obtain the asymptotic behaviour of the electric field in some regimes of physical interest.

Of particular relevance to what follows is that it was also shown there that a sufficient condition for the validity of this linearization is that
\[ \nu E_{\text{max}}^2 \ll 1, \tag{19} \]
where $E_{\text{max}}$ is an upper bound on the values attained by $|E(x)|$ on the interval $0 \leqslant x \leqslant 1$. Note that $E_{\text{max}}$ is not known until after the solution is (approximately) determined, so that (19) is an à posteriori consistency check on the applicability of the linearization, rather than an indicator of when it can be applied.

More recently, it has been shown [25, 27] that in any solution of the BVP as defined by (3) and (6), both $c_+(x)$ and $c_-(x)$ are positive for $0 \leqslant x \leqslant 1$. Moreover, at least one of $\Phi_+$, $\Phi_-$ is negative. Furthermore, it is now known that a unique solution exists for the reformulated BVP, and hence for the BVP as originally formulated for (3), for any given boundary values as in (6) and (8) [24–26].

As a result of these studies, it follows that every such solution falls into one of the following classes:

$$(A): E(x) > 0, \quad E'(x) < 0, \quad c_-(x) > c_+(x) > 0 \quad \text{for} \quad 0 < x < 1,$$

and $c_1 E(1)/c_0 > E(0) > E(1), \quad \Phi_- < 0, \quad \Phi_- < \Phi_+ = -\Phi_-$; \quad (20)

$$(B): E(x) < 0, \quad E'(x) > 0, \quad c_+(x) > c_-(x) > 0 \quad \text{for} \quad 0 < x < 1,$$

and $c_1 E(1)/c_0 < E(0) < E(1), \quad \Phi_+ < 0, \quad \Phi_+ < \Phi_- = -\Phi_+$; \quad (21)

$$(C): \quad E(x) = 0, \quad c_+(x) = c_-(x) = c_0 + (c_1 - c_0)x = c(x), \quad \text{say},$$

for $0 \leqslant x \leqslant 1, \quad \text{with} \quad \Phi_+ = \Phi_- = c_0 - c_1$. \quad (22)

It can be seen from (4) that in any such solution, $j > 0$ implies $\Phi_- < 0$, and $j < 0$ implies $\Phi_+ < 0$, while $j = 0$ implies both $\Phi_- < 0$ and $\Phi_+ < 0$; but these constraints are not enough to determine the class to which the solution belongs.

Note that it follows from (20) and (21) that for any solution in class A or B, $E_{\text{max}}^2$ in the sufficient condition (19) is given by $E(0)^2$.

The one solution in class C, which is discussed in the next section as Planck’s exact solution, is a solution of the BVP in the case when

$$j = (\tau_+ - \tau_-)(c_0 - c_1) = j_0, \quad \text{say}. \quad (23)$$

4. Series expansion

As noted in the introduction, approximate solutions of the reformulated BVP (14) and (15), and close variants of it, have been sought previously [17–19] in the form of asymptotic series. That approach involves expanding $E(x)$ in powers of $\nu$, and requires the tools of singular perturbation theory and matched asymptotic expansions [22], as can be seen from the fact that $\nu$ appears in (14) multiplying the highest derivative of $E(x)$. The zeroth order term in the (outer) expansion so obtained is given by a formula for $E(x)$ first obtained by Planck [2], in the limiting case where $\nu \to 0$ (the ‘infinite charge limit’).

This formula forms part of Planck’s approximate solution of the BVP in that limit. Written in dimensionless form, this approximate solution has $c_+(x) = c_-(x) = c(x)$ as in (22), and

$$E(x) = (\Phi_+ - \Phi_-)/2c(x), \quad \Phi_\pm = 2\tau_\pm(c_0 - c_1) \pm j. \quad (24)$$

It is more important for what follows that, as can easily be checked, (24) defines an exact solution (22) of the BVP for any non-zero value of $\nu$, in the particular case when $j = j_0$ as in (23).
Our approach is to hold $\nu$ fixed at some non-zero value, and look for a series expansion in a different parameter, perturbing away from Planck’s exact solution (22). Thus we seek a solution of (14) for the case

$$j = j_0 + \epsilon j_1 = (\tau_+ - \tau_-)(\epsilon_0 - \epsilon_1) + \epsilon j_1, \quad (25)$$

in the form

$$E(x) = 0 + \epsilon E_1(x) + \epsilon^2 E_2(x) + \cdots, \quad (26)$$

and write $E^{(\nu)}(x)$ for the series truncated after the term $\epsilon^n E_n(x)$. Here $\epsilon$ is a book-keeping parameter that can be set equal to 1 after calculations are completed. What is relevant in the perturbation (25) is the value of $\epsilon j_1$.

We note firstly from (26) that

$$E(x)E(y)^2 = V(x, y) = \epsilon^3 V_3(x, y) + \epsilon^4 V_4(x, y) + \cdots, \quad (29)$$

where

$$V_n(x, y) = E_1(x)U_{n-1}(y) + E_2(x)U_{n-2}(y) + \cdots + E_{n-2}(x)U_2(y), \quad (30)$$

for $n = 3, 4, \ldots$. Similarly

$$E(x) = 0 + \epsilon E_1(x) + \epsilon^2 E_2(x) + \cdots \quad (27)$$

where $U_2(x) = E_1(x)^2$, and

$$U_{2n}(x) = 2E_1(x)E_{2n-1}(x) + 2E_2(x)E_{2n-2}(x) + \cdots + 2E_{n-1}(x)E_n(x) + E_n(x)^2,$$

$$U_{2n-1}(x) = 2[E_1(x)E_{2n-2}(x) + E_2(x)E_{2n-3}(x) + \cdots + E_{n-1}(x)E_n(x)], \quad (28)$$

for $n = 2, 3, \ldots$. The ODE (14) can now be written with the help of (22) and (25) as

$$\nu E''(x) = 2\epsilon(x)E(x) + \frac{1}{2}\nu [V(x, 0) - V(x, 1)] - V(x, 0) + V(x, x)]$$

$$- 2\epsilon j_1 + \frac{1}{2}\nu(\tau_+ - \tau_-)[U(0) - U(1)]. \quad (31)$$

We now substitute in the series expansions of $E$, $U$, and $V$, and equate terms of equal degree in $\epsilon$. At $\epsilon^1$ we get

$$\nu E_1''(x) - 2\epsilon E_1(x) = -2j_1 = R_1, \quad \text{say}; \quad (32)$$

at $\epsilon^2$

$$\nu E_2''(x) - 2\epsilon E_2(x) = \frac{1}{2}\nu(\tau_+ - \tau_-)[U_2(0) - U_2(1)] = R_2, \quad (33)$$

and at $\epsilon^n$ for $n \geq 3$,

$$\nu E_n''(x) - 2\epsilon E_n(x) = R_n(x), \quad (34)$$

where

$$R_n(x) = \frac{1}{2}\nu \left\{ [V_n(x, 0) - V_n(x, 1)] - V_n(x, 0) + V_n(x, x) \right\}$$

$$+ (\tau_+ - \tau_-)[U_n(0) - U_n(1)] . \quad (35)$$
The ODEs (32), (33) and (15).

Note that each $R_n$ depends only on the $E_k(x), k < n$, determined at previous steps, so that each ODE takes the form of an Airy equation with known inhomogeneous RHS, thus permitting a solution for $E_n(x), E_n'(x)$ at each stage in the form

$$E_n(x) = \mathcal{F}_{R_n}(x), \quad E_n'(x) = \mathcal{G}_{R_n}(x),$$

(36)
as shown in appendix B. From (12) and (13) we can then obtain series expansions for the remaining unknowns $c_{\pm}(x), \Phi_{\pm}$.

Note from (B.7) that

$$\epsilon_n E_n(x) = F_{\epsilon_n} R_n(x), \quad \epsilon_n E_n'(x) = G_{\epsilon_n} R_n(x).$$

(37)
The approximate solution obtained in this way for the BVP of interest, up to order $\epsilon$, is

$$c_{\pm}^{(1)}(x) = c_0 + (c_1 - c_0)x + \epsilon \frac{1}{2} \nu \mathcal{G}_{j_0}(x),$$

$$c_{\pm}^{(1)}(x) = c_0 + (c_1 - c_0)x - \epsilon \frac{1}{2} \nu \mathcal{G}_{j_0}(x),$$

$$E^{(1)}(x) = \epsilon \mathcal{F}_{j_0}(x),$$

$$\Phi^{(1)}_{+} = c_0 - c_1 + \epsilon j_1, \quad \Phi^{(1)}_{-} = c_0 - c_1 - \epsilon j_1.$$  (38)

Noting (25) and (B.7), we can rewrite these formulas as

$$c_{\pm}^{(1)}(x) = c_0 + (c_1 - c_0)x + \frac{1}{2} \nu \mathcal{G}_{j_0-j}(x),$$

$$c_{\pm}^{(1)}(x) = c_0 + (c_1 - c_0)x - \frac{1}{2} \nu \mathcal{G}_{j_0-j}(x),$$

$$E^{(1)}(x) = \mathcal{F}_{j_0-j}(x),$$

$$\Phi^{(1)}_{+} = c_0 - c_1 - j_0 + j, \quad \Phi^{(1)}_{-} = c_0 - c_1 + j_0 - j.$$  (39)

It is not hard to check that this is, in dimensionless form, the approximate solution of the BVP (3) and (6) with $j_0$ as in (23), as obtained previously [10] by linearizing (14), neglecting the quadratic and cubic terms on the RHS.

5. Numerical evaluation of the series

MATLAB [45] was used to conduct a variety of numerical experiments, comparing the ‘exact’ numerical solution of (3) with the approximate solution obtained by terminating the series in (26) at order $\epsilon^n$ for a variety of values $n$, for various values of the dimensionless model parameters in the ranges

$$0 < \nu \leq 10, \quad 0 < \tau_+ (= 1 - \tau_-) < 1, \quad 0 < c_0 (= 1 - c_1) < 1,$$

$$\text{and} \quad -2.75 < j (= j_0 + \epsilon j_1) < 2.75.$$  (40)

It is important to emphasize at this point that in this paper we are primarily interested in the mathematical structure of the model of binary electrodiffusion defined in sections 2–4, rather than in the associated physics, which has been extensively discussed elsewhere in the literature [3–6, 9–11, 18, 46]. For this reason, we consider $\nu, \tau_+, c_0$ and $j$ as real parameters in the ranges (40), without regard for additional constraints imposed by the physics of particular experimental situations. For example, while values of $\nu$ less than 1 have commonly been
described in the literature just cited, in particular for nerve membranes [7, 8], a value as large as 10 corresponds to a ratio of internal Debye length to junction width δ of about 3.2. Rati-values greater than 1 have also been discussed in the literature, particularly in the context of the so-called ‘constant field approximation’, [39, 47–49]. They can be achieved in principle by making the junction width δ or the characteristic (reference) concentration c_ref in (A2) sufficiently small, without compromising charge-neutrality at junction boundaries. Having said that, we recognize that it may be difficult to achieve ratios as large as 3.2 in practice. Similar remarks apply to the values of the current-density J that are implied when our dimensionless |j| is allowed to reach values as large as 2.75. Such values of ν and |j| together will be found to give rise to values of |E_{max}| as large as 5.5, as in cases associated with figure 6 below for example, and so to electric field values (in dimensional form) as large as

\[ |E_{\text{max}}| \approx 5.5 k_B T/\varepsilon_0, \]  

leading to |E_{\text{max}}| δ \approx 5 \times 10^{-4} \text{ statVolt} \approx 150 \text{ mV} for monovalent ions at room temperatures. Depending on the value of δ, field strengths of that magnitude may be very much larger than those readily achieved in experiments.

Our justification for admitting such parameter values in the numerical experiments that follow, is that we wish to throw as much new light as possible on the mathematical model of electrodiffusion and its perturbation series solution. To that end we explore a wide range of mathematically sensible values of the parameters therein.

In what follows, \( S^{\text{num}} \) denotes the numerical solution with components \( c^{\text{num}}(x), E^{\text{num}}(x) \), etc and \( S^{(n)} \) denotes the nth approximation with components \( c^{(n)}(x), E^{(n)}(x) \), etc. Here \( c^{(n)}(x) \) and \( \Phi^{(n)}(x) \) are obtained from \( E^{(n)}(x) \) and \( E^{(n)}(x) \) using (12) and (13). (An abuse of notation is allowed below: the values of the components of \( S^{(n)} \) appearing there are actually approximations to the theoretical formulas of section 4, obtained using numerical evaluation of the integrals involved in appendix B.)

As remarked earlier, the modified BVP (14) and (15) is not straightforward to solve directly for \( E^{\text{num}}(x) \) by numerical methods [26], partly because of the complication mentioned earlier, that the coefficients in the ODE (14) are not all known \( \alpha \) priori. This difficulty is circumvented by returning to the original BVP, rewriting it as a system of five rather than three ODEs,

\[
\begin{align*}
\nu E^{(n)}(x) &= c^{-}(x) - c^{+}(x), \\
E^{(n)}(x) &= -E^{(n)}(x) c^{-}(x) - \Phi^{+}(x), \\
c^{+}(x) &= c^{+}(x) - c^{-}(x), \\
\Phi^{+}(x) &= 0, \\
\Phi^{-}(x) &= 0
\end{align*}
\]  

(42)

for \( 0 < x < 1 \), with BCs

\[
\begin{align*}
c^{+}(0) &= c^{-}(0) = c_0, \\
c^{+}(1) &= c^{-}(1) = c_1, \\
\tau^{+} \Phi^{+}(0) - \tau^{-} \Phi^{-}(0) &= j.
\end{align*}
\]  

(43)

This is now in a standard form, easily handled by MATLAB [45] library routines, which return numerical solutions for the unknown functions, including \( E^{\text{num}}(x) \) and \( E^{\text{num}}(x) \), almost instantaneously.

In all the examples in the next section, we take as a measure of the error in the \( n \)-th approximation

\[
\Delta_n = \max \left\{ \left| E^{(n)}(x) - E^{\text{num}}(x) \right| + \left| E^{(n)}(x) - E^{\text{num}}(x) \right| \right\},
\]  

(44)

bearing in mind that all components of \( S^{(n)} \) can be constructed from \( E^{(n)}(x) \) and \( E^{(n)}(x) \) using (12) and (13). Here the maxima are taken over the set of 1001 node points \( x = 0, 0.001, 0.002, \ldots, 0.999 \), 1 used in determining the ‘exact’ numerical solution \( S^{\text{num}} \).
We considered also the alternative error measure
\[ \Delta_n = \left( \int_0^1 \left\{ \left[ E^{(n)}(x) - E^{\text{num.}}(x) \right]^2 + \left[ E^{(n)\prime}(x) - E^{\text{num.}\prime}(x) \right]^2 \right\} \, dx \right)^{1/2}, \] (45)

but found no substantial differences in values or behaviour between \( \Delta_n \) and \( \Delta_n^* \) in the examples treated. Because numerical evaluation of the integral in (45) at each value of \( n \) introduces further small errors, use of \( \Delta_n \) was preferred in what follows.

The determination of the discretized \( E^{\text{num.}} \) and \( E^{\text{num.}\prime} \), and of the integrals involved in the determination of the discretized \( E^{(n)} \) and \( E^{(n)\prime} \), are all subject to numerical errors. Adopting a conservative position, we do not claim reliability of calculated values of \( \Delta_n \) smaller than \( 10^{-7} \), nor do we consider such values for \( n > 500 \). In each example below, we say only that the sequence of approximations \( S^{(n)}(x) \) appears to converge to \( S^{\text{num.}}(x) \) if a positive integer \( n_7 \) can be found such that \( \Delta_n < 10^{-7} \) for \( n > n_7 \), out to \( n = 500 \), and that it appears to diverge if the size of \( \Delta_n \) is clearly growing in size for sufficiently large \( n \)-values, out to \( n = 500 \).

5.1. Examples

In the first set of examples, \( \tau_+ = 1 - \tau_- = 0.6 \) and \( c_0 = 1 - c_1 = 1/3 \), so that according to (23),
\[ j_0 = -1/15 \approx -0.067. \] (46)

With these values held fixed, various values of \( \nu \) and \( \epsilon j_1 \) were considered, and in each case the error \( \Delta_n \) was calculated for increasing values of \( n \).

Figure 1 shows a plot in the case with \( \nu = 0.1, \epsilon j_1 = -0.5, \tau_+ = 0.6, c_0 = 1/3 \).

\[ \text{Figure 1. Plot of } E^{(1)}(x) \text{ (circles) and } E^{\text{num.}}(x) \text{ (solid line), showing fair agreement, in the case with } \nu = 0.1, \epsilon j_1 = -0.5, \tau_+ = 0.6, c_0 = 1/3. \]

(We considered also the alternative error measure
\[ \bar{\Delta}_n = \left( \int_0^1 \left\{ \left[ E^{(n)}(x) - E^{\text{num.}}(x) \right]^2 + \left[ E^{(n)\prime}(x) - E^{\text{num.}\prime}(x) \right]^2 \right\} \, dx \right)^{1/2}, \]

but found no substantial differences in values or behaviour between \( \bar{\Delta}_n \) and \( \Delta_n \) in the examples treated. Because numerical evaluation of the integral in (45) at each value of \( n \) introduces further small errors, use of \( \Delta_n \) was preferred in what follows.)

The determination of the discretized \( E^{\text{num.}} \) and \( E^{\text{num.}\prime} \), and of the integrals involved in the determination of the discretized \( E^{(n)} \) and \( E^{(n)\prime} \), are all subject to numerical errors. Adopting a conservative position, we do not claim reliability of calculated values of \( \Delta_n \) smaller than \( 10^{-7} \), nor do we consider such values for \( n > 500 \). In each example below, we say only that the sequence of approximations \( S^{(n)}(x) \) appears to converge to \( S^{\text{num.}}(x) \) if a positive integer \( n_7 \) can be found such that \( \Delta_n < 10^{-7} \) for \( n > n_7 \), out to \( n = 500 \), and that it appears to diverge if the size of \( \Delta_n \) is clearly growing in size for sufficiently large \( n \)-values, out to \( n = 500 \).

5.1. Examples

In the first set of examples, \( \tau_+ = 1 - \tau_- = 0.6 \) and \( c_0 = 1 - c_1 = 1/3 \), so that according to (23),
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With these values held fixed, various values of \( \nu \) and \( \epsilon j_1 \) were considered, and in each case the error \( \Delta_n \) was calculated for increasing values of \( n \).

Figure 1 shows a plot in the case \( n = 1, \nu = 0.1 \) and \( \epsilon j_1 = -0.5 \) (so that \( \epsilon |j_1/j_0| = 7.5 \)).

The ‘exact’ numerical solution \( E^{\text{num.}}(x) \) is shown as a solid line, and values of the first series approximation \( E^{(1)}(x) \) are shown at 21 evenly spaced values of \( x \) between \( x = 0 \) and \( x = 1 \), and marked o.

Figure 2 shows, for the same settings, plots of \( c^{\text{num.}}_\pm(x) \), \( c^{(1)}_\pm(x) \), \( \Phi^{\text{num.}}_\pm \) and \( \Phi^{(1)}_\pm \). It can be seen from the plots and (21) that this case belongs to class B. In this example, \( \nu E^{\text{max.}}_0 \approx 0.13 \) (see figure 1), so that the sufficient condition (19) is well-satisfied.
Accordingly, the numerical solution and this crudest \( n = 1 \) nontrivial approximation (39)—the linear approximation proposed in [10, 11]—show fair agreement, with \( \Delta_1 \approx 0.02 \).

Figure 3 on the left and in the centre shows the decrease of \( \log_{10} \Delta_n \) with increasing \( n \), until exceedingly small values are reached. (Nothing should be read into the apparent constancy of the error \( \Delta_n \) at values smaller than \( 10^{-10} \) for \( n > 10 \), which is presumably a computational artifact. As remarked above, estimates smaller than \( 10^{-7} \) should be regarded as unreliable. Similar remarks apply to figures 4 and 5 below.) We find \( \Delta_n < 10^{-7} \) for \( n > n_7 = 2 \) and \( \Delta_n < 10^{-7} \) for \( n > n_7 = 7 \), remaining so out to \( n = 500 \), and accordingly claim the the
sequence of approximations \( S^{(n)} \) appears to converge in this case to the solution of the BVP defined by (3) and (6).

Figure 3 on the right shows plots of \( E_{\text{num}}(x) \) and \( E^{(8)}(x) \), showing the excellent agreement implied by the size of \( \Delta_8 \). Corresponding excellent agreement of \( c^{(8)}(x) \) and \( \Phi^{(8)}(x) \) with \( E_{\text{num}}(x) \) and \( \Phi_{\text{num}}(x) \) follows, so we do not show the plots.

Lest the reader conclude that the apparent convergence here is a consequence of the fact that in this particular example \( \nu \ll 1 \) and \( \nu E_{\text{max}}^2 \ll 1 \) (so that \( |\epsilon_1/j_0| = 15 \)). Figure 4 on the left and in the centre shows plots of \( \log_{10} \Delta_n \) versus \( n \) out to \( n = 500 \), with in this case \( \Delta_1 \approx 0.049 \), \( \Delta_n < 10^{-3} \) for \( n > n_1 = 4 \) and \( \Delta_n < 10^{-7} \) for \( n > n_7 = 11 \), out to \( n = 500 \). Figure 4 on the right shows plots of \( E_{\text{num}}(x) \) and \( E^{(12)}(x) \), showing the excellent agreement implied by the size of \( \Delta_{12} \), and showing that this case also belongs to class B. Not only is \( \nu > 1 \) here, but in addition \( \nu E_{\text{max}}^2 \approx 4.5 \) (see figure 4), well outside the regime defined by (19), so the apparent convergence in this case is more surprising.

Consider also the case where \( \nu = 3.5 \) and \( \epsilon_1 = 2.0 \) (so that \( \epsilon_1/j_0 = 30 \)). Figure 5 on the left and in the centre shows plots of \( \log_{10} \Delta_n \) out to \( n = 500 \), and in this case \( \Delta_1 \approx 0.17 \), \( \Delta_n < 10^{-3} \) for \( n > n_3 = 10 \) and \( \Delta_n < 10^{-7} \) for \( n > n_7 = 43 \), out to \( n = 500 \). Figure 5 on the right shows plots of \( E_{\text{num}}(x) \) and \( E^{(44)}(x) \), showing the excellent agreement implied by the size of \( \Delta_{44} \), and also showing that this case belongs to class A.

Figure 5 also shows that \( \Delta_n \) does not decrease monotonically with increasing \( n \) in every case. In the previous two cases, the decrease is monotonic out to \( n = n_7 \), but here that is clearly not so. Numerous experiments show that this non-monotonic behaviour appears to be common, rather than exceptional.
Table 1 shows results from the above three cases and three other apparently convergent cases. Here as above, \( n_3 \) denotes the value of \( n \) beyond which the error \( \Delta_n \) falls below \( 10^{-3} \), and \( n_7 \) the value beyond which it falls below \( 10^{-7} \) and remains so, out to \( n = 500 \).

A variety of examples including those in table 1 suggests that for the chosen values of \( \tau_+ \) and \( c_0 \), apparent convergence occurs for any value of \( \nu \) in the range \( 0 < \nu \leq 10 \) (the largest value considered) provided \( |\epsilon_j| < 2.4 \), but typically becomes slower for a given value of \( \nu \) as \( |\epsilon_j| \) increases towards a value in the neighbourhood of 2.5, and eventually fails.

Consider for example the behaviour of the error in the following cases (all in class A) with \( \nu = 2.0 \), as illustrated in figure 6. When \( \epsilon_j_1 = 2.45 \), then \( n_7 = 265 \) and the error continues to decrease (non-monotonically) out to \( n = 500 \). When \( \epsilon_j_1 = 2.48 \), the situation is similar, but now \( n_7 = 413 \). When \( \epsilon_j_1 = 2.50 \), the error is still greater than \( 10^{-7} \) at \( n = 500 \), though it is apparently still decreasing non-monotonically. When \( \epsilon_j_1 = 2.53 \), the error is still greater than \( 10^{-7} \) at \( n = 500 \), and its behaviour for larger values of \( n \) is unclear. When \( \epsilon_j_1 = 2.56 \), the error decreases non-monotonically until \( n \approx 110 \), where it has a value \( \Delta_{110} \approx 5 \times 10^{-3} \), then starts to increase non-monotonically. These results suggest that when \( \nu = 2.0 \), breakdown of convergence occurs when \( \epsilon_j_1 \) increases to a value somewhere between 2.48 and 2.56.

The reader might suggest, after considering figure 6 in particular, that the series is divergent in all of these cases—and indeed, perhaps in every case—and that in the apparently convergent cases, sufficiently large values of \( n \) have not been considered to show that this is so. Another possibility, in our view unlikely, is that the perturbation expansion is providing an asymptotic sequence of approximations to the exact solution in every case, and that this sequence gives the best possible approximation for a particular value of \( n \), say \( n = n^* \), with \( n^* \approx 110 \) in the case \( \epsilon_j_1 = 2.56 \) for example, while \( n^* > 500 \) is unknown in the apparently convergent cases. Our numerical experiments are unable to decide among these possibilities, just as they are unable to prove convergence in any given case.
Also shown in the caption for figures 6 are the corresponding values of \( \nu E_{\text{max}}^2 \) and also of \( \Delta_1 \), the maximum error in the first approximation with \( n = 1 \). One of the biggest surprises in the results of this paper, strikingly illustrated by these examples, is the apparent lack of importance of the condition \( \nu E_{\text{max}}^2 \ll 1 \) of (19) in determining whether or not the series appears to converge. This is despite the apparent importance of the size of \( \nu E_{\text{max}}^2 \) in determining the accuracy of the ‘linear approximation’ of [11], corresponding to \( n = 1 \) here, which is reflected in the increase in the value of \( \Delta_1 \) with increasing value of the corresponding \( \nu E_{\text{max}}^2 \), as is clear from the numbers shown in the captions. Note however that for all the curves in figures 6 and 7, \( \Delta_1 < 1 \) even though \( \nu E_{\text{max}}^2 \gg 1 \), which is also a surprise.

Consider also the behaviour in the following cases (all in class B) with \( \nu = 1 \). When \( \epsilon_1 = -2.45 \), then \( n_7 = 262 \) and the error continues to decrease (non-monotonically) out to \( n = 500 \). When \( \epsilon_1 = -2.48 \), the situation is similar, but now \( n_7 = 414 \). When \( \epsilon_1 = -2.49 \), the error is still greater than \( 10^{-7} \) at \( n = 500 \), though it is apparently still decreasing non-monotonically. When \( \epsilon_1 = -2.55 \), the error decreases non-monotonically until it reaches a value of approximately \( 2.7 \times 10^{-3} \) when \( n \approx 135 \), then starts to increase non-monotonically, much as in the previous examples illustrated in figures 6. These results suggest in turn that when \( \nu = 1.0 \), breakdown of convergence occurs when \( \epsilon_1 \) decreases to a value between \(-2.49 \) and \(-2.55 \).

### Table 1. Some apparently convergent examples with \( \tau_+ = 0.6 \), \( \tau_- = 0.4 \), \( c_0 = 1/3 \) and \( c_1 = 2/3 \).

| \( \nu \) | \( \epsilon_1 \) | \( \nu E_{\text{max}}^2 \) | \( \Delta_1 \) | \( n_3 \) | \( n_7 \) | Class |
|---|---|---|---|---|---|---|
| 0.1 | -0.5 | 0.13 | 0.013 | 2 | 7 | B |
| 0.5 | 1.5 | 5.2 | 0.13 | 6 | 21 | A |
| 1.1 | -1.0 | 4.5 | 0.049 | 4 | 11 | B |
| 2.5 | -2.0 | 38 | 0.16 | 11 | 42 | B |
| 3.5 | 2.0 | 61 | 0.17 | 10 | 43 | A |
| 10.0 | 1.0 | 42 | 0.044 | 3 | 12 | A |

Figure 6. Plots of \( \log_{10} \Delta_n \) versus \( n \), out to \( n = 500 \), in cases with \( \nu = 2.0 \), \( \tau_+ = 0.6 \) and \( c_0 = 1/3 \), and with (from bottom upwards) \( \epsilon_1 = 2.45, 2.48, 2.50, 2.53 \) and 2.56. Corresponding values of \( \nu E_{\text{max}}^2 \) are 53, 55, 56, 57 and 58, with \( \Delta_1 \approx 0.14 \) in each case.
Examples like these suggest that the dominant influence on convergence is the value of $|\epsilon_j|$, but also that the value of $\nu$ plays a minor role. It has not been possible to determine what, if any, is the critical combination of those values.

The examples above all have $\tau_+ + c_0 = 0.6$ and $c_0 = 1/3$, and the situation is more complicated when other values of $\tau_+ (= 1 - \tau_-)$ and $c_0 (= 1 - c_1)$ are allowed, as it seems that the values of these constants also play roles in determining when the series (apparently) converges. For example, with $\nu = 2.0$, $\tau_+ = 0.6$, $c_0 = 1/3$, and $\epsilon_j = 2.45$, the series appears to converge when $\Delta_n(0)$ or $\Delta_n(1)$ versus $n$ in various ranges, in the case with $\nu = 2.0$, $\tau_+ = 0.6$, $c_0 = 1/3$, and $\epsilon_j = 2.45$, illustrating condition Q.

Figure 7. Plots of the errors $\Delta_n(0)$ (dot-solid) and $\Delta_n(1)$ (solid) versus $n$ in various ranges, in the case with $\nu = 2.0$, $\tau_+ = 0.6$, $c_0 = 1/3$, and $\epsilon_j = 2.45$, illustrating condition Q.

In trying to determine what combination(s) of the parameters $\nu$, $\epsilon_j$, $\tau_+ (= 1 - \tau_-)$ and $c_0 (= 1 - c_1)$ in the model governs (apparent) convergence, one is faced with a ‘tyranny of dimensionless constants’ [50]—in this case a 4-dimensional parameter-space that has proved too large to explore fully by numerical experiments. Similar difficulties face efforts to determine when the error $\Delta_n$ decreases monotonically with increasing $n$, and when it does not.

5.2. Behaviour of the error

In order to examine more closely the peculiar oscillatory behaviour of the error revealed above, even in apparently convergent cases, we consider separately now the behaviour of the errors in the $n$th approximations $E^{(n)}(x)$ and $E^{(n)\prime}(x)$ to the field and its derivative, and
Figure 8. Plots of the errors $\Delta_n(0)$ (dot-solid) and $\Delta_n(1)$ (solid) versus $n$ in the case with $\nu = 1.0$, $\tau_+ = 0.6$, $c_0 = 1/3$, and $\epsilon_j = -2.45$, illustrating the failure of condition Q at $n = 8$.

differently weighted sums of those errors, beyond that assumed in the definition of $\Delta_n$ in (44). To this end, set

$$\Delta_n(w) = \max \left\{ 2w \left| E^{(n)}(x) - E^{\text{num}}(x) \right| + 2(1 - w) \left| E^{(n)'}(x) - E^{\text{num}'}(x) \right| \right\},$$

(47)

where the maximum is taken over the discrete values of $x$ as in (44), and $0 \leq w \leq 1$ is a weight factor at our disposal. Note that the measure $\Delta_n$ used previously is now given by $\Delta_n(0.5)$, and that separate measures of the errors in $E^{(n)}(x)$ and $E^{(n)'}(x)$ are given by $\Delta_n(1)$ and $\Delta_n(0)$, respectively. Note also that if $\Delta_n(w)$ decreases to values less than $10^{-7}$ out to $n = 500$, for some fixed value $0 < w < 1$, then we can reasonably extend our claim of apparent convergence of the sequences of approximations to both $E^{\text{num}}(x)$ and $E^{\text{num}'}(x)$.

The values of $\Delta_n(1)$ and $\Delta_n(0)$ were computed for $1 \leq n \leq n_7 + 1$, for each of the apparently convergent cases in table 1, and for the cases with $\nu = 2$ and $\epsilon_j = 2.45$ and $2.48$ also discussed in section 5.1. In each of these cases, it was found that condition Q holds, where

**Condition Q.** For all $1 \leq n \leq n_7 + 1$, whenever $\Delta_{n+1}(1) > \Delta_n(1)$, then $\Delta_{n+1}(0) < \Delta_n(0)$ and whenever $\Delta_{n+1}(0) > \Delta_n(0)$, then $\Delta_{n+1}(1) < \Delta_n(1)$.

This unexpected reciprocity may hold a clue to the convergence properties of the expansion. All these cases have $\tau_+ (= 1 - \tau_-) = 0.6$ and $c_0 (= 1 - c_1) = 1/3$. The condition also holds in the case with $\nu = 1$, $\tau_+ = 0.5$, $c_0 = 1/3$ and $\epsilon_j = -2.5$ mentioned above. Figure 7 illustrates this remarkable behaviour in the case with $\nu = 2.0$ and $\epsilon_j = 2.45$, where it holds for $1 \leq n \leq n_7 + 1 = 267$, as already mentioned, while the errors oscillate repeatedly in this range during their decline to values below $10^{-7}$.

Condition Q does not hold for all apparently convergent cases. It fails for the cases with $\nu = 1.0$, $\tau_+ = 0.6$, $c_0 = 1/3$ and $\epsilon_j = -2.45$ or $-2.48$, also discussed in section 5.1, although only at a few isolated values of $n$ in each case. Figure 8 shows the errors in the first of these cases for $1 \leq n \leq 10$, showing that $\Delta_9(1) > \Delta_8(1)$ and also $\Delta_9(0) > \Delta_8(0)$. The condition also fails to hold for the case with $\nu = 1.0$, $\tau_+ = 0.9$, $c_0 = 1/3$ and $\epsilon_j = -2.10$, and the case with $\nu = 1$, $\tau_+ = 0.6$, $c_0 = 0.2$ and $\epsilon_j = -2.15$, both mentioned in section 5.1 and both apparently convergent.

Despite these exceptions, one is led from the cases when condition Q does hold to consider the possibility that a suitably weighted measure (47) of the overall error might in each
apparently convergent case decline more smoothly towards zero than (44), perhaps even monotonically, with the weighted up-and-down variations in $\Delta_n(1)$ and $\Delta_n(0)$ partially cancelling each other.

Further numerical experiments show that a monotonic decline in the value of $\Delta_n(w)$ to less than $10^{-7}$ for $n > n_f$ does indeed occur in the first, third, fifth and sixth cases in table 1, with $w = 0.5, 0.5, 0.25$ and 0.2 respectively. In the first two of these, the weighting is just as in (44), and the decline in the measure of the overall error in the field and its derivative was already seen to be monotonic in figures 3 and 4. Figure 9 shows the graphs of $\Delta_n(0.25)$ versus $n$ for $1 \leq n \leq 15$ and $16 \leq n \leq 44$ for the fifth case in table 1 (see figure 5), showing how the choice $w = 0.25$ leads to a monotonically declining measure of the overall error in this case.

It is not clear what to conclude from these numerical results. We make the

**Conjecture.** If it is possible to choose a weighting $0 < w < 1$ in a given apparently convergent case that makes the measure of error $\Delta_n(w)$ decrease monotonically to values less than $10^{-7}$, out to $n = 500$, then the sequence of approximations $S^{(n)}(x)$ does converge to the exact solution of the BVP in that case.

This leaves aside the question as to what happens in other apparently convergent cases.

### 6. Concluding remarks

When the approximation to the solution of (14) was first obtained [10, 11] by linearizing the ODE to a form of Airy’s equation—as remarked above, this corresponds to the first term in the formal series solution described in section 4—the value of the result was twofold. Firstly, it provided an approximate but explicit expression for the field $E(x)$, enabling comparisons with earlier, cruder approximations, and clarifying the physics of the electrodiffusion process. Secondly, from the expression obtained for $E(x)$, the asymptotic behaviour of the field was determined approximately at vanishingly small values of the current density $j$. This was achieved using the known asymptotic behaviour of Airy functions [16], providing further important information about the physics of the situation in that regime.

In these days of fast and reliable numerical computations which enable the solution of the BVP defining the model to be obtained with great accuracy, a series expansion like (26)
with increasingly complicated expressions for the successive terms, is of limited value as a means of defining better approximations than those previously obtained—even arbitrarily good approximations—to the solution of what is a complicated nonlinear problem. On the other hand, the expansion may have considerable theoretical significance in revealing an expression for the Painlevé transcendent satisfying (14) as a convergent (or asymptotic) series, constructed using Airy functions, for a wide range of values of the constants appearing in that equation.

A rigorous mathematical examination of the properties of this series will be needed to determine its convergence properties, because they cannot be confirmed by numerical experiments of the type used above, however suggestive they may be. This applies in particular to the problem of establishing the truth or otherwise of the conjecture made at the end of the preceding section.

In this context, it is worth remarking again, and may be crucial, that for the BCs described by (6) and (8), the many numerical experiments that have been considered all suggest strongly that the solution of the BVP, including the Painlevé transcendent electric field $E(x)$, is free from singularities in the region $0 \leq x \leq 1$ of interest.

### Appendix A. Dimensionless variables

Assuming constant boundary values for (1),

\[ \hat{c}_+(0) = \hat{c}_-(0) = \hat{c}_0, \quad \hat{c}_+(\delta) = \hat{c}_-(\delta) = \hat{c}_1 > \hat{c}_0, \quad (A.1) \]

we introduce the constant reference concentration $c_{\text{ref.}} = \hat{c}_0 + \hat{c}_1$ and the dimensionless constant

\[ \nu = \frac{\epsilon k_B T}{4\pi (ze)^3 \delta^3 c_{\text{ref.}}} \quad (A.2). \]

Then (1) and (2) are made dimensionless by setting

\[ x = \hat{x}/\delta, \quad c_\pm(x) = \hat{c}_\pm(\hat{x})/c_{\text{ref.}} \]

\[ E(x) = \frac{(ze\delta/k_B T) \hat{E}(\hat{x})}{(A.3)} \]

and

\[ \Phi_\pm = \bar{\Phi}_\pm \delta/c_{\text{ref}} D_\pm, \quad J = \frac{\delta}{(ze)c_{\text{ref}}(D_+ + D_-)} \tilde{J}. \quad (A.4) \]

Setting

\[ \tau_\pm = D_\pm/(D_+ + D_-) \quad (A.5) \]

we obtain (3) and (4).

### Appendix B. Airy boundary-value problems

Consider the linear BV problem

\[ \nu y'''(x) = 2c(x) y(x) + R(x), \quad y'(0) = 0 = y'(1), \quad (B.1) \]

where $R(x)$ is given, continuous on the interval $[0, 1]$, and $c(x)$ is as defined in (22).

Linearly-independent solutions of the homogeneous ODE ($R = 0$) are provided by
where $A_i$ and $B_i$ are Airy functions of the first and second kind \cite{15,16}. Note that $s > 0$ for all $0 \leq x \leq 1$, and that $A_i(s)$ and $B_i(s)$ are both positive for $s > 0$. Thus $A(x)$ and $B(x)$ are both positive for $0 \leq x \leq 1$.

Because the Wronskian of $A_i$ and $B_i$ is equal to $1/\pi$, that of $A$ and $B$ is given by

$$W = A(x)B'(x) - B(x)A'(x) = \left[2(\epsilon_1 - \epsilon_0)/(\pi^2 \nu)\right]^{1/3}, \tag{B.3}$$

and the general solution of ODE in (B.1), according to the method of variation of parameters \cite{13}, is then

$$y(x) = -\frac{1}{\nu W} \left\{A(x) \int_0^x R(y)B(y) \, dy - B(x) \int_0^x R(y)A(y) \, dy \right\} + d_A A(x) + d_B B(x). \tag{B.4}$$

with $d_A$, $d_B$ arbitrary constants. Imposing the BCs in (B.1) then gives

$$d_A = \frac{B'(0)}{[A'(1)B'(0) - A'(0)B'(1)] \nu W} \left\{A'(1) \int_0^1 R(y)B(y) \, dy - B'(1) \int_0^1 R(y)A(y) \, dy \right\},$$

$$d_B = -\frac{A'(0)}{[A'(1)B'(0) - A'(0)B'(1)] \nu W} \left\{A'(1) \int_0^1 R(y)B(y) \, dy - B'(1) \int_0^1 R(y)A(y) \, dy \right\}. \tag{B.5}$$

We write the solution $y(x)$ so defined as $F_R(x)$ to emphasize its dependence on the inhomogeneous term $R(x)$.

We note also from (B.4) that

$$y'(x) = -\frac{1}{\nu W} \left\{A'(x) \int_0^x R(y)B(y) \, dy - B'(x) \int_0^x R(y)A(y) \, dy \right\} + d_A A'(x) + d_B B'(x) \tag{B.6}$$

and, with $d_A$, $d_B$ as in (B.5), write this function $y'(x)$ as $G_R(x)$. Finally, we note from the form of (B.4)–(B.6) that

$$e F_R(x) = F_{eR}(x), \quad e G_R(x) = G_{eR}(x). \tag{B.7}$$

for any constant $e$.

**ORCID iDs**

A J Bracken \(\text{https://orcid.org/0000-0001-5181-4483}\)

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