

# A Planck's derivation of an equation for the liquid junction potential

The following provides a summary of the reasoning of Max Planck in his 1890 work on liquid junction potentials for an arbitrary number of species.<sup>1</sup> Here we have not consulted other sources recounting this derivation and are re-formulating our own direct translation of this work into our symbolic terminology.

From the Nernst-Planck equations, we have for positive ions  $i$  and negative ions  $j$ :

$$D_i \left( \frac{\partial^2 C_i}{\partial x^2} + f \frac{\partial}{\partial x} \left( C_i \frac{\partial \phi}{\partial x} \right) \right) - \frac{\partial C_i}{\partial t} = 0 \quad (\text{A.1})$$

$$D_j \left( \frac{\partial^2 C_j}{\partial x^2} - f \frac{\partial}{\partial x} \left( C_j \frac{\partial \phi}{\partial x} \right) \right) - \frac{\partial C_j}{\partial t} = 0 \quad (\text{A.2})$$

where  $f = F/RT$ .

The above may be summed:

$$\sum_i D_i \frac{\partial^2 C_i}{\partial x^2} + \sum_i f D_i \frac{\partial}{\partial x} \left( C_i \frac{\partial \phi}{\partial x} \right) - \frac{\partial}{\partial t} \sum_i C_i = 0 \quad (\text{A.3})$$

$$\sum_j D_j \frac{\partial^2 C_j}{\partial x^2} - \sum_j f D_j \frac{\partial}{\partial x} \left( C_j \frac{\partial \phi}{\partial x} \right) - \frac{\partial}{\partial t} \sum_j C_j = 0 \quad (\text{A.4})$$

If we assume that the solution is electroneutral under conditions of zero passed current, let:

$$\frac{\sigma}{2} = \sum_i C_i = \sum_j C_j \quad (\text{A.5})$$

and so, if:

$$I = \sum_i D_i C_i \quad (\text{A.6})$$

$$J = \sum_j D_j C_j \quad (\text{A.7})$$

by integration:

$$\frac{\partial \phi}{\partial x} = -\frac{1}{f} \frac{\partial(I-J)}{\partial x} \quad (\text{A.8})$$

Therefore if  $I$  and  $J$  may be established as functions of  $x$ , the above integrates across all space to give the potential difference across the junction.

Planck argued that a step function for  $I$  or  $J$  cannot be used in the above, as  $\partial I/\partial x$  is then zero everywhere except at the junction, where it is infinite. He therefore substituted the concept of a boundary layer of arbitrary thickness  $\delta$  outside of which all  $C_i$  and  $C_j$  remain constant and equal to their bulk values, and inside of which  $I$ ,  $J$ , and  $\phi$  take as yet unknown forms, which may have very large, but finite, spatial derivatives.

Further, Planck employed the physical insight that the experimentally observed liquid junction potential is steady, i.e. not a function of time, and assumed that this could only arise when the time derivatives of  $I$  and  $J$  inside the boundary layer were also zero - the inaccuracy here is implicit the assumption that the thickness  $\delta$  is a constant rather than a function of time.

Taking the Nernst-Planck equations at  $\partial C_i/\partial t = 0$  and  $\partial C_j/\partial t = 0$  allows the equations to be integrated to:

$$\frac{\partial C_i}{\partial x} + fC_i \frac{\partial \phi}{\partial x} = \lambda_i \quad (\text{A.9})$$

$$\frac{\partial C_j}{\partial x} - fC_j \frac{\partial \phi}{\partial x} = \lambda_j \quad (\text{A.10})$$

where  $\lambda_k$  are the constants of integration (in fact still formally functions of  $t$ , as Planck explains).

Summing the above, and so as long as the electroneutrality condition holds, if we define:

$$\Lambda_i = \sum_i \lambda_i \quad (\text{A.11})$$

$$\Lambda_j = \sum_j \lambda_j \quad (\text{A.12})$$

$$\sum_k \frac{\partial \sigma}{\partial x} = \Lambda_i + \Lambda_j \quad (\text{A.13})$$

and integrating:

$$\sigma = (\Lambda_i + \Lambda_j)x + \text{const.} \quad (\text{A.14})$$

i.e. a linear change in total concentration, such that:

$$(\sigma_R - \sigma_L) = \delta(\Lambda_i + \Lambda_j) \quad (\text{A.15})$$

so

$$\sigma = \sigma_L + \frac{\sigma_R - \sigma_L}{\delta} \cdot x \quad (\text{A.16})$$

Subtraction of Equation A.10 from Equation A.9 is also helpful:

$$f \cdot \sigma \cdot \frac{\partial \phi}{\partial x} = \Lambda_i - \Lambda_j \quad (\text{A.17})$$

and so by combination:

$$\frac{\partial \phi}{\partial x} = \frac{1}{f} \frac{(\Lambda_i - \Lambda_j)\delta}{(\sigma_R - \sigma_L) \cdot x + \sigma_L \delta} \quad (\text{A.18})$$

and integrating from 0 to  $\delta$  we find:

$$\Delta\phi_{\text{LJP}} = \frac{1}{f} \frac{(\Lambda_i - \Lambda_j)\delta}{(\sigma_R - \sigma_L)} \log \frac{\sigma_R}{\sigma_L} \quad (\text{A.19})$$

To determine the value of  $(\Lambda_i - \Lambda_j)$ , the following substitution is made:

$$\zeta = \left( \frac{\sigma_R}{\sigma_L} \right)^{\frac{(\Lambda_i - \Lambda_j)\delta}{(\sigma_R - \sigma_L)}} \quad (\text{A.20})$$

such that

$$\Delta\phi_{\text{LJP}} = \frac{1}{f} \log \zeta \quad (\text{A.21})$$

Multiplying each Equation A.9 and Equation A.10 by  $D_k$  and summing:

$$\sum_i D_i \lambda_i = \frac{\partial I}{\partial x} + f \cdot I \cdot \frac{\partial \phi}{\partial x} \quad (\text{A.22})$$

$$\sum_j D_j \lambda_j = \frac{\partial J}{\partial x} - f \cdot J \cdot \frac{\partial \phi}{\partial x} \quad (\text{A.23})$$

it follows from subtraction and then substitution of Equation A.8 that

$$\sum_i D_i \lambda_i = \sum_j D_j \lambda_j \equiv \Lambda_D \quad (\text{A.24})$$

This equality, together with Equation A.18, and the above, gives soluble ordinary differential equations for  $I$  and  $J$ , which result in the following identity for  $\zeta$ :

$$\frac{\zeta I_{\text{R}} - I_{\text{L}}}{J_{\text{R}} - \zeta J_{\text{L}}} = \frac{\log \frac{\sigma_{\text{R}}}{\sigma_{\text{L}}} - \log \zeta}{\log \frac{\sigma_{\text{R}}}{\sigma_{\text{L}}} + \log \zeta} \cdot \frac{\zeta \sigma_{\text{R}} - \sigma_{\text{L}}}{\sigma_{\text{R}} - \zeta \sigma_{\text{L}}} \quad (\text{A.25})$$

from which  $\log \zeta$  and hence the liquid junction potential are obtained by appropriate substitution of the system variables.

This transcendental equation is only applicable in cases where all ions have equal magnitudes of charge; the full Henderson equation, in the main text, was derived thermodynamically (not *via* diffusion-migration equations) by Henderson,<sup>2</sup> but that derivation rests heavily on the assumption of linearity of concentration profiles in a boundary layer, as introduced by Planck in the above. Henderson viewed this derivation of linearity, at least as concerns total ionic concentration, as generally proven (Henderson p. 120, “Es wird von Planck gezeigt, dass ganz allgemein die Gesamtkonzentration in der Grenzschicht ... linear durch dieselbe variiert.”), and linearity was applied to single ion concentrations by Henderson in his derivation (Henderson p. 121).<sup>2</sup>

Planck’s equation reduces to a form equivalent to the Henderson equation for Types 1 and 2. For Type 1, both sides of the junction have the same composition, and so:

$$I_{\text{L}} = D_i C_{\text{L}} \quad ; \quad I_{\text{R}} = D_i C_{\text{R}} \quad (\text{A.26})$$

$$J_{\text{L}} = D_j C_{\text{L}} \quad ; \quad J_{\text{R}} = D_j C_{\text{R}} \quad (\text{A.27})$$

and hence  $I_{\text{R}}/I_{\text{L}} = J_{\text{R}}/J_{\text{L}} = C_{\text{R}}/C_{\text{L}}$ .

On substitution into the above Equation A.25, noting that  $2C_{\text{R}} = \sigma_{\text{R}}$  and  $2C_{\text{L}} = \sigma_{\text{L}}$ :

$$\frac{D_i(\zeta C_{\text{R}} - C_{\text{L}})}{D_j(C_{\text{R}} - \zeta C_{\text{L}})} = \frac{\log \frac{C_{\text{R}}}{C_{\text{L}}} - \log \zeta}{\log \frac{C_{\text{R}}}{C_{\text{L}}} + \log \zeta} \cdot \frac{\zeta C_{\text{R}} - C_{\text{L}}}{C_{\text{R}} - \zeta C_{\text{L}}} \quad (\text{A.28})$$

and cancelling

$$\frac{D_i}{D_j} = \frac{\log \frac{C_{\text{R}}}{C_{\text{L}}} - \log \zeta}{\log \frac{C_{\text{R}}}{C_{\text{L}}} + \log \zeta} \quad (\text{A.29})$$

which rearranges straightforwardly to

$$\log \zeta = \frac{D_j - D_i}{D_j + D_i} \log \frac{C_R}{C_L} \quad (\text{A.30})$$

and on substitution into Equation A.21 then:

$$\Delta E_{\text{LJP}} = \frac{RT}{F} \frac{D_j - D_i}{D_j + D_i} \log \frac{C_R}{C_L} = \frac{D_A - D_X}{D_A + D_X} \frac{RT}{F} \log \frac{C_L}{C_R} \quad (\text{A.31})$$

which is the Type 1 Henderson equation.

For Type 2, both sides of the junction have the same total concentration, and so:

$$\sigma_R = \sigma_L \quad (\text{A.32})$$

and also due to the shared ion

$$J_R = J_L = D_j C \quad (\text{A.33})$$

and

$$I_R = D_{i,R} C = \frac{D_{i,R}}{D_{i,L}} I_L \quad (\text{A.34})$$

Substituting again into the above equation A.25, we find that:

$$\frac{D_{i,R} \zeta - D_{i,L}}{D_j(1 - \zeta)} = -\frac{\zeta - 1}{1 - \zeta} \quad (\text{A.35})$$

Again we cancel, and multiplying through by  $D_j(1 - \zeta)$  and rearranging:

$$\zeta = \frac{D_{i,L} + D_j}{D_{i,R} + D_j} \quad (\text{A.36})$$

so on substitution into Equation A.21 we recover:

$$\Delta E_{\text{LJP}} = \frac{RT}{F} \log \frac{D_{i,L} + D_j}{D_{i,R} + D_j} = \frac{RT}{F} \log \frac{D_A + D_X}{D_B + D_X} \quad (\text{A.37})$$

which is the Type 2 Henderson equation.

## B Details of numerical methods employed

### B.1 Space and time grids

The one-dimensional simulation space is divided into  $2n + 1$  points labelled  $X_{-n}, X_{-n+1}, \dots, X_0, \dots, X_n$ , with  $X_0 = 0$  being the central point. The grid corresponds to that used in the previous work using the NPP equation set,<sup>3</sup> with a region of an extremely dense regular grid spacing close to the centre, and expanding proportionally to  $X$  on each side beyond some characteristic point  $X_s$ , called the switching point. Mathematically, the position of a point  $X_i$  for positive  $i$  is defined as:

$$X < X_s : \quad X_i = X_{i-1} + \gamma_X \cdot X_s \quad (\text{B.1})$$

$$X \geq X_s : \quad X_i = X_{i-1} + \gamma_X \cdot X_{i-1} \quad (\text{B.2})$$

where  $\gamma_X$  is the grid expansion coefficient; for negative  $i$ ,  $X_{-i} = -X_i$ . Note that  $X_s$  cannot simply equal  $X_1$ , as it is important to have continuity of grid spacing at the point where the linear grid becomes an expanding grid. The time grid is defined using the same technique;  $\gamma_\tau$  and  $\tau_s$  denote the time grid expansion coefficient and the time switching point respectively. The choice of  $\gamma_\tau$  and  $\tau_s$  is only limited by the fact that the time step,  $\gamma_\tau \cdot t_s$  must be by at least five orders of magnitude smaller than the time by which the junction potential approaches its steady state value to obtain significant precision before the steady liquid junction potential is reached. The choice of  $\gamma_X$  and  $X_s$ , however, is a compromise between the simulation runtime and convergence criteria; in a convergence study at varying  $\gamma_\tau$ ,  $\tau_s$ ,  $\gamma_X$  and  $X_s$  it was found that the simulation convergence depends only on the two latter parameters. Optimal parameters found in this convergence study are:  $\gamma_\tau = 10^{-4}$ ,  $\tau_s = 10^{-2}$ ,  $X_s = 10^{-6}$  and  $\gamma_X$  between  $10^{-3}$  and  $5 \times 10^{-4}$ . These were used throughout the following and were found to be stable and converged within the range of liquid junction systems simulated.

A fully implicit discretisation of the time derivative is used; space derivatives used central differencing across the expanding grid. The resulting set of non-linear simultaneous equations is solved

using the iterative Newton-Raphson method.

## B.2 The iterative Newton-Raphson method

The iterative Newton-Raphson method is a standard numerical procedure for solving a system of coupled non-linear simultaneous equations.<sup>4</sup> The  $n$  equations are written in a homogeneous form:

$$f_n(x_0, x_1, \dots, x_n) = 0 \quad (\text{B.3})$$

Let  $\mathbf{x}$  be the vector containing the unknowns  $x_0$  to  $x_n$ ; let  $\mathbf{f}(\mathbf{x})$  be the vector containing the functions  $f_0$  to  $f_n$ ; and let  $\mathbf{u}$  be the vector containing the differences between  $\mathbf{x}$  at successive iterations, such that

$$\mathbf{u} = \mathbf{x}_{z+1} - \mathbf{x}_z \quad (\text{B.4})$$

In the simple Newton-Raphson method, the Taylor series of a function about a trial solution  $x_0$  is considered:

$$f(x) \approx f(x_0) + (x - x_0)f'(x_0) = 0 \quad (\text{B.5})$$

and hence the solution  $x$  may be derived from successive iterations of the form:

$$x_{z+1} = x_z - \frac{f(x_z)}{f'(x_z)} \quad (\text{B.6})$$

For a function of multiple variables, a trial vector  $\mathbf{x}_0$  may be altered similarly:

$$f(\mathbf{x}) \approx f(\mathbf{x}_0) + \sum_n (x_n - x_{n,0}) \frac{\partial f(\mathbf{x}_0)}{\partial x_n} \quad (\text{B.7})$$

and hence, defining  $u_n = x_n - x_{n,0}$

$$\sum_n u_n \frac{\partial f(\mathbf{x}_0)}{\partial x_n} = -f(\mathbf{x}_0) \quad (\text{B.8})$$

Where there are  $n$  simultaneous equations associated with the  $n$  variables, this may be extended, such that for each variable  $m$ :

$$\sum_n u_n \frac{\partial f_m(\mathbf{x}_0)}{\partial x_n} = -f_m(\mathbf{x}_0) \quad (\text{B.9})$$

which may be expressed for the vectors  $\mathbf{u}$  and  $\mathbf{f}$  in the matrix form:

$$\mathbf{J}(\mathbf{x}_0)\mathbf{u} = -\mathbf{f}(\mathbf{x}_0) \quad (\text{B.10})$$

where  $\mathbf{J}$  is the Jacobian matrix, being the  $n \times n$  square matrix for which the element  $J_{mn}$  is described:

$$J_{mn} = \frac{\partial f_m}{\partial x_n} \quad (\text{B.11})$$

Equation B.10 is solved iteratively and  $\mathbf{x}$  is augmented by  $\mathbf{u}$ , until all values  $u_0$  to  $u_n$  are less than a characteristic parameter  $\epsilon$ , at which point  $\mathbf{x}$  is taken as the trial vector for the next timestep.

Equation B.10 can be solved by an adapted Thomas algorithm method<sup>5</sup> (LU decomposition followed by back-substitution) as the Jacobian is a diagonal matrix, with a minimum of 9 non-zero diagonals for Type 1 or 13 non-zero diagonals for Type 2 when the unknowns  $x_n$  are appropriately ordered (e.g. for Type 1:  $c_{A,0}, \phi_0, c_{X,0}, c_{A,1}, \phi_1, c_{X,1}, \dots$  ).

## C Simulated liquid junction potentials

The plots below show the resulting limiting (pseudo-steady state) liquid junction potential resulting from simulation for various cases in Type 1 and Type 2, demonstrating close agreement with the Henderson equation. The definition of the limiting potential was where:

$$0.998 \cdot |\Delta\theta_{\text{LJP}}(\tau)| \leq |\Delta\theta_{\text{LJP}}(\tau/2)| \quad (\text{C.1})$$

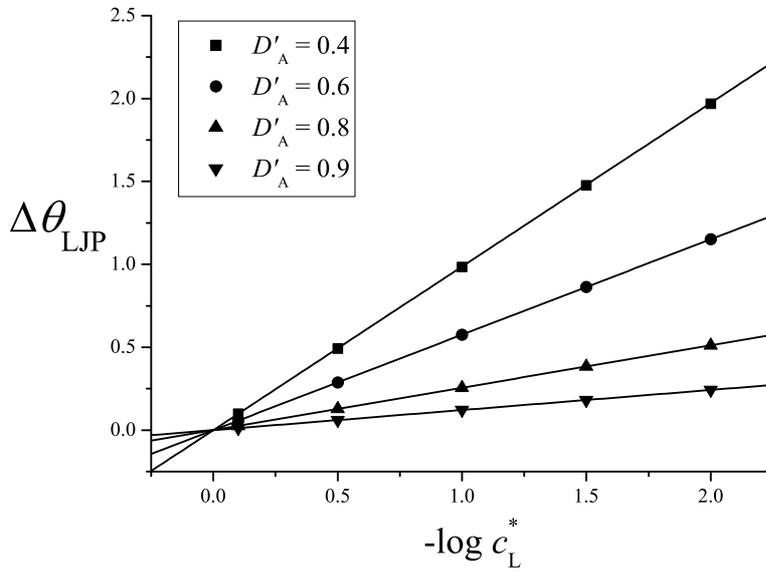


Figure 1: Comparison of simulated liquid junction potentials (symbols),  $\Delta\theta_{\text{LJP}}$ , at pseudo-steady state and the theoretical values given by the Henderson equation (lines), for a Type 1 system with varying  $D'_A$  and  $c_L^*$ .

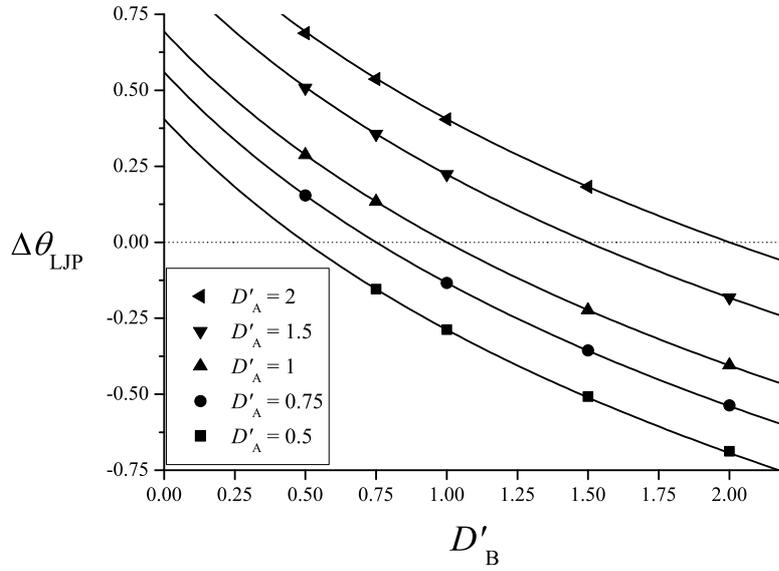


Figure 2: Comparison of simulated liquid junction potentials (symbols),  $\Delta\theta_{\text{LJP}}$ , at pseudo-steady state and the theoretical values given by the Henderson equation (lines), for a Type 2 system with varying  $D'_A/D_X$  and  $D'_B$ . The dotted line indicates  $D_A = D_B$ , where the liquid junction potential is undefined.

## D $\tau \rightarrow 0$ asymptotic analysis (Type 1)

To consider the limit  $\tau \rightarrow 0$ , we analyse the electric field arising from diffusion-only mass transport, ignoring the feedback of that field. The solution of the diffusion equation from the initial condition of a step function concentration profile is easily obtained by either Laplace transformation or Boltzmann analysis, and is well known.<sup>6</sup> If

$$c_i(X, \tau = 0) = \alpha + \beta \operatorname{sgn}(X) \quad (\text{D.1})$$

with  $\operatorname{sgn}(X)$  the sign function, defined as  $\operatorname{sgn}(X) = 1$  for  $X > 0$  and  $\operatorname{sgn}(X) = -1$  for  $X < 0$ , then the diffusion equation, i.e. Equation 2.14 at zero field, yields:

$$c_i(X, \tau) = \alpha + \beta \operatorname{erf} \left( \frac{X}{2\sqrt{D'_i\tau}} \right) \quad (\text{D.2})$$

where for consistency with our generic Type 1 junction, the constants  $\alpha$  and  $\beta$  are:

$$\alpha = \frac{1 + c_L^*}{2} \quad ; \quad \beta = \frac{1 - c_L^*}{2} \quad (\text{D.3})$$

Substitution into the Poisson equation yields:

$$\frac{\partial^2 \theta}{\partial X^2} = (c_X - c_A) \approx \beta \left( \operatorname{erf} \left( \frac{X}{2\sqrt{\tau}} \right) - \operatorname{erf} \left( \frac{X}{2\sqrt{D'_A\tau}} \right) \right) \quad (\text{D.4})$$

Integrating between  $X$  and  $-\infty$  with respect to  $X$  yields:

$$\frac{\partial \theta}{\partial X} - \frac{\partial \theta(-\infty)}{\partial X} = \frac{\partial \theta}{\partial X} \approx \beta \int_{-\infty}^X \left( \operatorname{erf} \left( \frac{X'}{2\sqrt{\tau}} \right) - \operatorname{erf} \left( \frac{X'}{2\sqrt{D'_A\tau}} \right) \right) dX' \quad (\text{D.5})$$

We therefore need to evaluate

$$\frac{\partial \theta}{\partial X} = \beta \int_{-\infty}^X \left( \operatorname{erf} \left( \frac{X'}{p} \right) - \operatorname{erf} \left( \frac{X'}{q} \right) \right) dX' \quad (\text{D.6})$$

where  $p = 2\sqrt{\tau}$  and  $q = 2\sqrt{D'_A\tau}$ . It is useful to note here the general result for the anti-derivative of an error function:

$$\operatorname{erf} \left( \frac{x}{a} \right) = \frac{d}{dx} \left( x \operatorname{erf} \left( \frac{x}{a} \right) + \frac{a}{\sqrt{\pi}} e^{-\frac{x^2}{a^2}} \right) \quad (\text{D.7})$$

such that

$$\int_{-\infty}^X \left( \operatorname{erf} \left( \frac{X'}{p} \right) - \operatorname{erf} \left( \frac{X'}{q} \right) \right) dX' = \left[ X' \left( \operatorname{erf} \left( \frac{X'}{p} \right) - \operatorname{erf} \left( \frac{X'}{q} \right) \right) + \frac{1}{\sqrt{\pi}} \left( p e^{-\frac{X'^2}{p^2}} - q e^{-\frac{X'^2}{q^2}} \right) \right]_{-\infty}^X \quad (\text{D.8})$$

The limit of this expression to  $-\infty$  must be evaluated:

$$\lim_{x \rightarrow -\infty} \left( x \left( \operatorname{erf}(x/p) - \operatorname{erf}(x/q) \right) + \frac{1}{\sqrt{\pi}} \left( p e^{-\frac{x^2}{p^2}} - q e^{-\frac{x^2}{q^2}} \right) \right) = \lim_{x \rightarrow -\infty} (x \left( \operatorname{erf}(x/p) - \operatorname{erf}(x/q) \right)) \quad (\text{D.9})$$

Applying l'Hôpital's rule:

$$\begin{aligned} \lim_{x \rightarrow -\infty} \frac{(\operatorname{erf}(x/p) - \operatorname{erf}(x/q))}{(1/x)} &= -\frac{2}{\sqrt{\pi}} \lim_{x \rightarrow -\infty} \frac{(1/p)e^{-\frac{x^2}{p^2}} - (1/q)e^{-\frac{x^2}{q^2}}}{(1/x^2)} \\ &= -\frac{2}{\sqrt{\pi}} \lim_{x \rightarrow -\infty} \frac{x^2}{(1/p)e^{\frac{x^2}{p^2}} - (1/q)e^{\frac{x^2}{q^2}}} \\ &= 0 \end{aligned} \quad (\text{D.10})$$

as any exponential necessarily becomes infinite faster than  $x^n$ .

Hence:

$$\frac{\partial \theta}{\partial X} = \beta \left( X \left( \operatorname{erf} \left( \frac{X}{p} \right) - \operatorname{erf} \left( \frac{X}{q} \right) \right) + \frac{1}{\sqrt{\pi}} \left( p e^{-\frac{X^2}{p^2}} - q e^{-\frac{X^2}{q^2}} \right) \right) \quad (\text{D.11})$$

The further integration of this function is required to recover the liquid junction potential.

$$\Delta \theta_{\text{LJP}} = \beta \int_{-\infty}^{\infty} \left( X \left( \operatorname{erf} \left( \frac{X}{p} \right) - \operatorname{erf} \left( \frac{X}{q} \right) \right) + \frac{1}{\sqrt{\pi}} \left( p e^{-\frac{X^2}{p^2}} - q e^{-\frac{X^2}{q^2}} \right) \right) dX = \beta I \quad (\text{D.12})$$

where the integral

$$\begin{aligned} I &= \int_{-\infty}^{\infty} \left( X \left( \operatorname{erf} \left( \frac{X}{p} \right) - \operatorname{erf} \left( \frac{X}{q} \right) \right) + \frac{1}{\sqrt{\pi}} \left( p e^{-\frac{X^2}{p^2}} - q e^{-\frac{X^2}{q^2}} \right) \right) dX \\ &= \int_{-\infty}^{\infty} X \left( \operatorname{erf} \left( \frac{X}{p} \right) - \operatorname{erf} \left( \frac{X}{q} \right) \right) dX + \frac{p^2}{2} (1 + \operatorname{erf}(\infty)) - \frac{q^2}{2} (1 + \operatorname{erf}(\infty)) \\ &= (p^2 - q^2) + \int_{-\infty}^{\infty} X \left( \operatorname{erf} \left( \frac{X}{p} \right) - \operatorname{erf} \left( \frac{X}{q} \right) \right) dX \end{aligned} \quad (\text{D.13})$$

Integrating the latter term by parts, we may note that the integral within the brackets (excluding  $X$ )

is that determined above, and so:

$$\begin{aligned}
I &= (p^2 - q^2) + \int_{-\infty}^{\infty} X \left( \operatorname{erf} \left( \frac{X}{p} \right) - \operatorname{erf} \left( \frac{X}{q} \right) \right) dX \\
&= (p^2 - q^2) + [X^2 \left( \operatorname{erf} \left( \frac{X}{p} \right) - \operatorname{erf} \left( \frac{X}{q} \right) \right) + \frac{X}{\sqrt{\pi}} \left( p e^{-\frac{X^2}{p^2}} - q e^{-\frac{X^2}{q^2}} \right)]_{-\infty}^{\infty} \\
&\quad - \int_{-\infty}^{\infty} X \left( \operatorname{erf} \left( \frac{X}{p} \right) - \operatorname{erf} \left( \frac{X}{q} \right) \right) + \frac{1}{\sqrt{\pi}} \left( p e^{-\frac{X^2}{p^2}} - q e^{-\frac{X^2}{q^2}} \right) dX
\end{aligned} \tag{D.14}$$

The leading expression evaluated at the limits  $X = \pm\infty$  is zero, from the same arguments made by l'Hôpital's rule above; the latter integral is simply  $I$ . Therefore:

$$\begin{aligned}
I &= (p^2 - q^2) - I \\
&= \frac{(p^2 - q^2)}{2}
\end{aligned} \tag{D.15}$$

and so

$$\begin{aligned}
\Delta\theta_{\text{LJP}} &= \beta I = \frac{\beta}{2}(p^2 - q^2) \\
&= (1 - c_{\text{L}}^*)(1 - D'_{\text{A}}) \cdot \tau
\end{aligned} \tag{D.16}$$

The point of maximum field occurs where  $c_{\text{A}} = c_{\text{X}}$ , as discussed in Section 3.2.2, which from Equations D.1 and D.2 is necessarily at  $X = 0$  for  $\tau > 0$ .

Substitution of  $X = 0$  into Equation D.11 yields:

$$\left. \frac{\partial\theta}{\partial X} \right|_{\text{max}} \approx \frac{1 - c_{\text{L}}^*}{\sqrt{\pi}} (1 - \sqrt{D'_{\text{A}}}) \cdot \sqrt{\tau} \tag{D.17}$$

which is plotted with Equation D.16 as the  $\tau \rightarrow 0$  asymptotes in Figure 2 (main text), with evident agreement in both cases with simulation in this limit.

The above analysis is in fact indistinguishable mathematically from the leading term analysis of a series solution in increasing powers  $\tau^i$  (as  $\tau \rightarrow 0$ ), and so analysis of the second term of this solution ought to reveal the  $\tau^{\frac{3}{2}}$  dependency of  $X_{\text{LJP}}$ , which is not accounted for by the above. The mathematics involved is substantially more complex than the above, however, and has been to date intractable. An empirical analysis of the slopes of various  $X_{\text{LJP}} = a \cdot \tau^{\frac{3}{2}}$  is therefore carried out.

Type 1 liquid junctions were simulated at low  $\tau$  for a variety of values of  $c_L^*$  and  $D'_A$ .  $X_{LJP} \propto \tau^{\frac{3}{2}}$  behaviour was observed as  $\tau \rightarrow 0$  in all cases, so the dependence and magnitude of the coefficient of proportionality was studied empirically. The coefficient of proportionality  $dX_{LJP}/d\tau^{\frac{3}{2}}$  was assessed by taking  $X_{LJP}/\tau^{\frac{3}{2}}$  at  $\tau = 10^{-2}$ , where asymptotic behaviour was observed in all cases. The dependence of this coefficient on the variables  $c_L^*$  and  $D'_A$  is shown below at Figures 1 and 2.

Inferring from these that the function then takes the form  $X_{LJP} = a \cdot (1 - c_L^*) D'_A{}^{\frac{3}{4}} \tau^{\frac{3}{2}}$ , the value of  $a$  was determined to be  $\approx -0.4$  by dividing the gradients through  $dX_{LJP}/d\tau^{\frac{3}{2}}$  by  $(1 - c_L^*) D'_A{}^{\frac{3}{4}}$  for all the simulations performed (Figure 3).

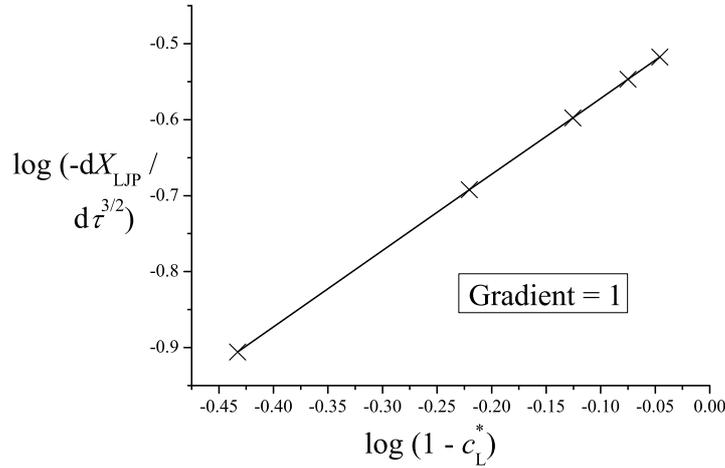


Figure 1: Logarithmic plot of  $dX_{LJP}/d\tau^{\frac{3}{2}}$  against  $(1 - c_L^*)$ , showing a linear dependency.

This reveals the following expression to hold:

$$X_{LJP} \approx -0.4 (1 - c_L^*) D'_A{}^{\frac{3}{4}} \tau^{\frac{3}{2}} \quad (\text{D.18})$$

which on substitution yields the following rationalised dimensional form:

$$x_{LJP} \approx 0.1 \left( \frac{1}{x_{\text{Debye,R}}^2} - \frac{1}{x_{\text{Debye,L}}^2} \right) (\sqrt{x_{\text{Diff,A}} \cdot x_{\text{Diff,X}}})^3 \quad (\text{D.19})$$

where the Debye lengths refer to the solutions at the two sides of the junction and are defined as at Equation 2.16, and  $x_{\text{Diff},i}$  is the characteristic diffusion length,  $= \sqrt{2D_i t}$ .

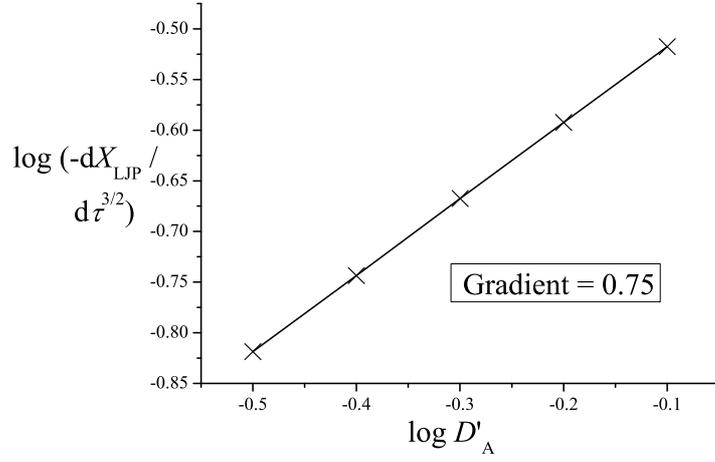


Figure 2: Logarithmic plot of  $dX_{LJP}/d\tau^{3/2}$  against  $D'_A$ , showing a  $3/4$ -power dependency.

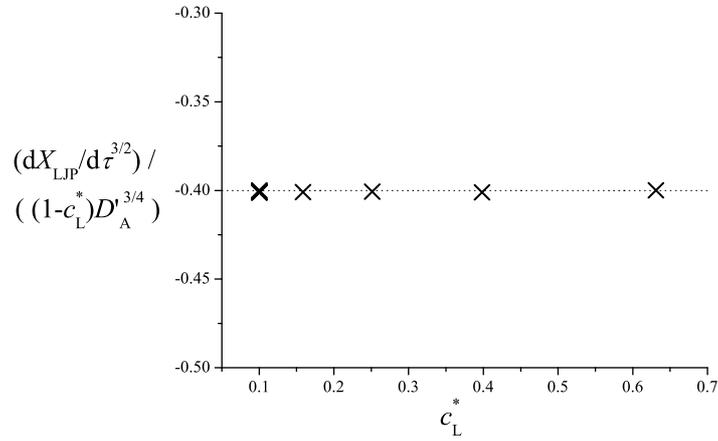


Figure 3: Logarithmic plot of  $(dX_{LJP}/d\tau^{3/2})/((1-c_L^*)D_A^{3/4})$  against  $c_L^*$ . Many values of  $D'_A$  were recorded at the point  $c_L^* = 0.1$ , so there is an overlap of points here.

## E $\tau \rightarrow 0$ asymptotic analysis (Type 2)

A similar analysis is applied for Type 2 systems in the limit  $\tau \rightarrow 0$ . The diffusion-only concentration profiles are again:

$$c_i(X, \tau = 0) = \alpha + \beta \operatorname{sgn}(X) \quad (\text{E.1})$$

Here, the mathematics is in fact simplified as the equimolar concentrations give  $\alpha_A = \alpha_B = 1/2$  and  $\beta_B = -\beta_A = 1/2$ . The species X may be ignored as it is uniformly concentrated at  $\tau = 0$  and hence its diffusive flux is zero.

Substitution into the Poisson equation then yields in this case:

$$\frac{\partial^2 \theta}{\partial X^2} = \frac{1}{2} \left( \operatorname{erf} \left( \frac{X}{2\sqrt{D'_A \tau}} \right) - \operatorname{erf} \left( \frac{X}{2\sqrt{D'_B \tau}} \right) \right) \quad (\text{E.2})$$

which is the same problem as the Type 1 case but with:

$$\beta = \frac{1}{2} \quad ; \quad p = 2\sqrt{D'_A \tau} \quad ; \quad q = 2\sqrt{D'_B \tau} \quad (\text{E.3})$$

and so the same solutions (in  $\beta, p, q$ ) apply, the derivation being detailed as before in Supporting Information D. The result for the electric field is Equation D.11, and the liquid junction potential is:

$$\begin{aligned} \Delta\theta_{\text{LJP}} &= \frac{p^2 - q^2}{4} \\ &= (D'_A - D'_B) \cdot \tau \end{aligned} \quad (\text{E.4})$$

The liquid junction position again occurs to the first approximation at  $X = 0$ , which on substitution into Equation D.11 yields the time-dependent expression for electric field:

$$\left. \frac{\partial \theta}{\partial X} \right|_{\text{max}} \approx \frac{1}{\sqrt{\pi}} (\sqrt{D'_A} - \sqrt{D'_B}) \cdot \sqrt{\tau} \quad (\text{E.5})$$

# F Boltzmann transformation of the Nernst-Planck-Poisson equations

The Boltzmann transformation<sup>7</sup> was introduced by Ludwig Boltzmann in 1894 to assist in the solution of the diffusion equation when  $D(x)$  is not constant; he applied a substitution  $z = x/\sqrt{t}$  to the diffusion equation to find solutions in this form. The following summarises and clarifies its application to the Nernst-Planck-Poisson equations in order to facilitate a long  $\tau$  asymptotic analysis, as introduced by Hickman.<sup>8</sup>

For the general case of a species  $k$  with charge  $z_k$  and normalised diffusion coefficient  $D'_k$ , the dimensionless Nernst-Planck-Poisson equations are:

$$D'_k \left( \frac{\partial^2 c_k}{\partial X^2} + z_k \frac{\partial}{\partial X} (c_k \xi) \right) - \frac{\partial c_k}{\partial \tau} = 0 \quad (\text{F.1})$$

$$\frac{\partial \xi}{\partial X} + \sum_k z_k c_k = 0 \quad (\text{F.2})$$

where  $\xi$  represents the dimensionless potential gradient  $= (\partial\theta/\partial X)$ .

The Boltzmann transformation  $(X, \tau) \rightarrow (z, u)$  is applied, where:

$$z = \frac{X}{\sqrt{\tau}} \quad (\text{F.3})$$

$$u = \frac{1}{\tau} \quad (\text{F.4})$$

and so

$$\frac{\partial f}{\partial X} = u^{\frac{1}{2}} \frac{\partial f}{\partial z} \quad (\text{F.5})$$

$$\frac{\partial f}{\partial \tau} = -\frac{uz}{2} \frac{\partial f}{\partial z} - u^2 \frac{\partial f}{\partial u} \quad (\text{F.6})$$

Therefore the transformed equations are:

$$D'_k \left( u \frac{\partial^2 c_k}{\partial z^2} + z_k u^{\frac{1}{2}} \frac{\partial}{\partial z} (c_k \xi) \right) + \frac{uz}{2} \frac{\partial c_k}{\partial z} + u^2 \frac{\partial c_k}{\partial u} = 0 \quad (\text{F.7})$$

$$u^{\frac{1}{2}} \frac{\partial \xi}{\partial z} + \sum_k z_k c_k = 0 \quad (\text{F.8})$$

The substitution  $\eta = \xi u^{\frac{1}{2}}$  is used here; additionally we may divide through by  $u$  in the first equation:

$$D'_k \left( \frac{\partial^2 c_k}{\partial z^2} + z_k \frac{1}{u} \frac{\partial}{\partial z} (c_k \eta) \right) + \frac{z}{2} \frac{\partial c_k}{\partial z} + u \frac{\partial c_k}{\partial u} = 0 \quad (\text{F.9})$$

or alternatively and equivalently

$$\frac{\partial^2 c_k}{\partial z^2} + z_k \frac{1}{u} \frac{\partial}{\partial z} (c_k \eta) + \frac{1}{D'_k} \left( \frac{z}{2} \frac{\partial c_k}{\partial z} + u \frac{\partial c_k}{\partial u} \right) = 0 \quad (\text{F.10})$$

and

$$\frac{\partial \eta}{\partial z} + \sum_k z_k c_k = 0 \quad (\text{F.11})$$

## G $\tau \rightarrow \infty$ asymptotic analysis (Type 1)

The following is a brief summary of work by Hickman<sup>8</sup> and Jackson<sup>9</sup> on  $\tau \rightarrow \infty$  asymptotic analysis of the Type 1 case, followed by extended analysis of their results in the context of junction motion, and comparison with simulation.

The Nernst-Planck-Poisson equations are first Boltzmann transformed (Supporting Information F) into the new variables  $z$  and  $u$ , where:

$$z = \frac{X}{\sqrt{\tau}} \quad ; \quad u = \frac{1}{\tau} \quad (\text{G.1})$$

The Boltzmann transformed forms of the NPP equations for a Type 1 system are:

$$\frac{\partial^2 c_A}{\partial z^2} + \frac{1}{u} \frac{\partial}{\partial z} (c_A \eta) + \frac{1}{D'_A} \left( \frac{z}{2} \frac{\partial c_A}{\partial z} + u \frac{\partial c_A}{\partial u} \right) = 0 \quad (\text{G.2})$$

$$\frac{\partial^2 c_X}{\partial z^2} - \frac{1}{u} \frac{\partial}{\partial z} (c_X \eta) + \frac{1}{D'_X} \left( \frac{z}{2} \frac{\partial c_X}{\partial z} + u \frac{\partial c_X}{\partial u} \right) = 0 \quad (\text{G.3})$$

$$\frac{\partial \eta}{\partial z} + c_A - c_X = 0 \quad (\text{G.4})$$

where a dimensionless potential gradient (negative electric field)  $\eta$  has been used:

$$\eta = \frac{\partial \theta}{\partial z} \quad (\text{G.5})$$

These may be reformulated to new equations (G.2)+(G.3) and (G.2)-(G.3) in terms of a total ionic strength  $\sigma$  and a charge density  $\rho$ :

$$\sigma = c_A + c_X \quad (\text{G.6})$$

$$\rho = c_A - c_X \quad (\text{G.7})$$

and hence

$$\frac{\partial^2 \sigma}{\partial z^2} + \frac{1}{u} \frac{\partial}{\partial z} (\rho \eta) + \delta_1 \left( \frac{z}{2} \frac{\partial \sigma}{\partial z} + u \frac{\partial \sigma}{\partial u} \right) + \delta_2 \left( \frac{z}{2} \frac{\partial \rho}{\partial z} + u \frac{\partial \rho}{\partial u} \right) = 0 \quad (\text{G.8})$$

$$\frac{\partial^2 \rho}{\partial z^2} + \frac{1}{u} \frac{\partial}{\partial z} (\sigma \eta) + \delta_2 \left( \frac{z}{2} \frac{\partial \sigma}{\partial z} + u \frac{\partial \sigma}{\partial u} \right) + \delta_1 \left( \frac{z}{2} \frac{\partial \rho}{\partial z} + u \frac{\partial \rho}{\partial u} \right) = 0 \quad (\text{G.9})$$

$$\frac{\partial \eta}{\partial z} + \rho = 0 \quad (\text{G.10})$$

where if  $D_X$  is chosen as the normal diffusion coefficient, then:

$$\delta_1 = \frac{\frac{1}{D'_A} + 1}{2} \quad ; \quad \delta_2 = \frac{\frac{1}{D'_A} - 1}{2} \quad (\text{G.11})$$

The following forms are then assumed for  $\sigma(z, u)$ ,  $\rho(z, u)$ , and  $\eta(z, u)$ :

$$f(z, u) = \sum_{i=0}^{\infty} f_i(z) u^i \quad (\text{G.12})$$

implying that as  $\tau \rightarrow \infty$  and hence  $u \rightarrow 0$ , all but the leading terms will vanish and so the asymptotic solution consists exclusively of the leading non-zero terms.

Then:

$$\sum_{i=0}^{\infty} \frac{d^2 \sigma_i}{dz^2} u^i + \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \frac{d(\rho_i \eta_j)}{dz} u^{i+j-1} \quad (\text{G.13})$$

$$+ \delta_1 \sum_{i=0}^{\infty} \left( \frac{z}{2} \frac{d\sigma_i}{dz} u^i + i\sigma_i u^i \right) + \delta_2 \sum_{i=0}^{\infty} \left( \frac{z}{2} \frac{d\rho_i}{dz} u^i + \frac{i\rho_i}{u} \right) = 0$$

$$\sum_{i=0}^{\infty} \frac{d^2 \rho_i}{dz^2} u^i + \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \frac{d(\sigma_i \eta_j)}{dz} u^{i+j-1} \quad (\text{G.14})$$

$$+ \delta_2 \sum_{i=0}^{\infty} \left( \frac{z}{2} \frac{d\sigma_i}{dz} u^i + i\sigma_i u^i \right) + \delta_1 \sum_{i=0}^{\infty} \left( \frac{z}{2} \frac{d\rho_i}{dz} u^i + \frac{i\rho_i}{u} \right) = 0$$

$$\sum_{i=0}^{\infty} \frac{d\eta_i}{dz} u^i + \sum_{i=0}^{\infty} \rho_i u^i = 0 \quad (\text{G.15})$$

These expressions generate terms in  $u^{-1}, u^0, \dots$ , and the homogeneous nature of the equations allows us to collect the coefficients of each power of  $u$  and state that their sum equals zero, such that the equations above are zero at *all*  $u$ . The terms in  $u^{-1}$  and the Poisson equation in  $u^0$  give:

$$\frac{d(\rho_0 \eta_0)}{dz} = 0 \quad (\text{G.16})$$

$$\frac{d(\sigma_0 \eta_0)}{dz} = 0 \quad (\text{G.17})$$

$$\frac{d\eta_0}{dz} + \rho_0 = 0 \quad (\text{G.18})$$

Direct application of the boundary conditions reveals that  $\eta_0 = 0$ . If  $\eta_0(z)$  is non-zero,  $\xi_0(z) = \eta_0(z)\sqrt{\tau} \rightarrow \infty$  at  $\tau \rightarrow \infty$ .  $\xi_0(z) = 0$  at  $|z| = \infty$ , however, so if  $\eta_0(z)$  is non-zero at  $|z| < \infty$  then  $\partial\xi_0/\partial z \rightarrow \infty$  as  $z \rightarrow \infty$ , which is inconsistent with the Poisson equation as the charge density  $\rho$  is confined to zero at this boundary. Hence  $\eta_0 = 0$  and the above are then limited to the statement that:

$$\rho_0 = 0 \tag{G.19}$$

This leading term electroneutrality in solutions of the NPP equations was implied by the outer asymptotic analysis performed for the Donnan equilibrium problem by MacGillivray.<sup>10</sup>

Then equating coefficients of the following powers gives, for all  $i$  from  $i = 0$  to  $\infty$ :

$$\begin{aligned} \frac{d^2\sigma_i}{dz^2} + \sum_{j=0}^{i+1} \frac{d(\rho_j\eta_{1+i-j})}{dz} \\ + \delta_1 \left( \frac{z}{2} \frac{d\sigma_i}{dz} + i\sigma_i \right) + \delta_2 \left( \frac{z}{2} \frac{d\rho_i}{dz} + i\rho_i \right) = 0 \end{aligned} \tag{G.20}$$

$$\begin{aligned} \frac{d^2\rho_i}{dz^2} + \sum_{j=0}^{i+1} \frac{d(\sigma_j\eta_{1+i-j})}{dz} \\ + \delta_2 \left( \frac{z}{2} \frac{d\sigma_i}{dz} + i\sigma_i \right) + \delta_1 \left( \frac{z}{2} \frac{d\rho_i}{dz} + i\rho_i \right) = 0 \end{aligned} \tag{G.21}$$

$$\frac{d\eta_{i+1}}{dz} + \rho_{i+1} = 0 \tag{G.22}$$

For the initial case that  $i = 0$  above (powers of  $u^0$ , and of  $u^1$  for the Poisson equation), and substituting  $\rho_0 = \eta_0 = 0$ , we find:

$$\frac{d^2\sigma_0}{dz^2} + \delta_1 \frac{z}{2} \frac{d\sigma_0}{dz} = 0 \tag{G.23}$$

$$\frac{d}{dz}(\sigma_0\eta_1) + \delta_2 \frac{z}{2} \frac{d\sigma_0}{dz} = 0 \tag{G.24}$$

$$\frac{d\eta_1}{dz} + \rho_1 = 0 \tag{G.25}$$

Solution of the former two of this set is sufficient to provide an asymptotic limit which agrees with the Henderson equation for the Type 1 case.

First let us consider Equation G.23 as it is a straightforward ordinary differential equation in one function. Choice of a suitable integrating factor yields:

$$\frac{d}{dz} \left( e^{\frac{\delta_1 z^2}{4}} \frac{d\sigma_0}{dz} \right) = 0 \quad (\text{G.26})$$

and hence integrating yields

$$\frac{d\sigma_0}{dz} = \lambda e^{-\frac{\delta_1 z^2}{4}} \quad (\text{G.27})$$

If now we integrate with respect to  $z$  between  $z$  and  $-\infty$ , where  $\sigma_0 = 2c_L^*$  from the boundary conditions:

$$\sigma_0(z) - 2c_L^* = \lambda \sqrt{\frac{\pi}{\delta_1}} \left( 1 + \operatorname{erf} \left( \frac{z\sqrt{\delta_1}}{2} \right) \right) \quad (\text{G.28})$$

and evaluating at  $z = +\infty$ :

$$\begin{aligned} \sigma_0(\infty) = 2 &= 2c_L^* + \lambda \sqrt{\frac{\pi}{\delta_1}} (1 + \operatorname{erf}(\infty)) \\ &= 2 \left( c_L^* + \lambda \sqrt{\frac{\pi}{\delta_1}} \right) \end{aligned} \quad (\text{G.29})$$

and hence

$$\lambda = (1 - c_L^*) \sqrt{\frac{\delta_1}{\pi}} \quad (\text{G.30})$$

$$\begin{aligned} \sigma_0(z) &= 2c_L^* + (1 - c_L^*) \left( 1 + \operatorname{erf} \left( \frac{z\sqrt{\delta_1}}{2} \right) \right) \\ &= (1 + c_L^*) + (1 - c_L^*) \operatorname{erf} \left( \frac{z\sqrt{\delta_1}}{2} \right) \\ &= 2 \left( \alpha + \beta \operatorname{erf} \left( \frac{z\sqrt{\delta_1}}{2} \right) \right) \end{aligned} \quad (\text{G.31})$$

and

$$\frac{d\sigma_0}{dz} = 2\beta \sqrt{\frac{\delta_1}{\pi}} e^{-\frac{z^2 \delta_1}{4}} \quad (\text{G.32})$$

Substitution into Equation G.24:

$$\frac{d}{dz} (\sigma_0 \eta_1) = -\delta_2 \beta z \sqrt{\frac{\delta_1}{\pi}} e^{-\frac{z^2 \delta_1}{4}} \quad (\text{G.33})$$

and as  $\eta_1(-\infty) = 0$

$$\begin{aligned}
\sigma_0 \eta_1 &= 2\beta \frac{\delta_2}{\delta_1} \sqrt{\frac{\delta_1}{\pi}} \int_{-\infty}^z \left( -\frac{\delta_1}{2} z' e^{-\frac{z'^2 \delta_1}{4}} \right) dz' \\
&= 2\beta \frac{\delta_2}{\delta_1} \sqrt{\frac{\delta_1}{\pi}} \int_{-\infty}^z \frac{d}{dz'} \left( e^{-\frac{z'^2 \delta_1}{4}} \right) dz' \\
&= 2\beta \frac{\delta_2}{\delta_1} \sqrt{\frac{\delta_1}{\pi}} e^{-\frac{z^2 \delta_1}{4}}
\end{aligned} \tag{G.34}$$

and so

$$\eta_1 = \frac{\beta \delta_2}{\sqrt{\delta_1 \pi}} \cdot \frac{e^{-\frac{z^2 \delta_1}{4}}}{\alpha + \beta \operatorname{erf}\left(\frac{z\sqrt{\delta_1}}{2}\right)} = \frac{\delta_2}{\delta_1} \cdot \frac{\frac{d\sigma_0}{dz}}{\sigma_0} \tag{G.35}$$

The  $\tau \rightarrow \infty$  behaviour of the system of the electric field is then well characterised by:

$$\xi \approx \eta_1(z) \cdot u \cdot u^{-\frac{1}{2}} = \frac{\eta_1(z)}{\sqrt{\tau}} \tag{G.36}$$

excluding all following terms as vanishing in this limit. Comparison of the this predicted long  $\tau$  electric field with simulation shows excellent agreement (Figure 1).

The liquid junction potential may be determined by the integration of  $\eta_1$ , which is achieved as follows

$$\begin{aligned}
\Delta\theta_{\text{LJP}} &= \int_{-\infty}^{\infty} \eta_1(z) dz \\
&= \frac{\delta_2}{\delta_1} \int_{-\infty}^{\infty} \frac{\frac{d\sigma_0}{dz}}{\sigma_0} dz \\
&= \frac{\delta_2}{\delta_1} [\ln |\sigma_0|]_{-\infty}^{\infty} \\
&= \frac{\delta_2}{\delta_1} \ln \left| \frac{\alpha + \beta \operatorname{erf}(\infty)}{\alpha + \beta \operatorname{erf}(-\infty)} \right| \\
&= \frac{\delta_2}{\delta_1} \ln \left| \frac{\alpha + \beta}{\alpha - \beta} \right| \\
&= \frac{\delta_2}{\delta_1} \ln \left| \frac{\gamma + 1}{\gamma - 1} \right|
\end{aligned} \tag{G.37}$$

where  $\gamma = (\alpha/\beta)$ . On re-dimensionalisation this recovers the Type 1 Henderson equation (Equation 1.2, main text) precisely, without any recourse to dynamic electroneutrality or linear concentration profiles anywhere in the above.

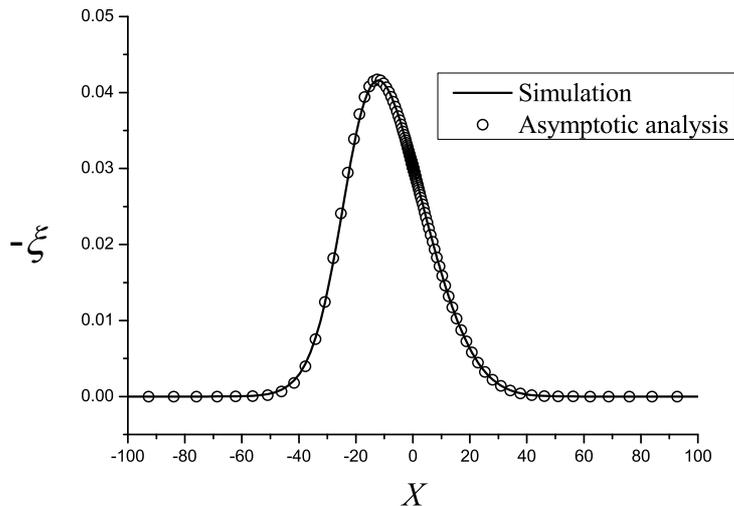


Figure 1: Comparison of the simulated electric field for the model HCl system,  $-\xi$ , at long time ( $\tau = 100\tau_{\text{trs}}$ ) with the leading non-zero term,  $-\xi_1$ , in the asymptotic analysis introduced by Hickman and Jackson.

This concludes a summary of work on the Type 1 case in Hickman<sup>8</sup> and Jackson,<sup>9</sup> but a closer analysis of the asymptotic field is of interest here. To the first order of approximation, the field is maximum where  $d\eta_1/dz = -\rho_1 = 0$ , neglecting the trivial cases  $z = \pm\infty$ . Differentiation of the simplified expression in Equation G.35 using the quotient rule gives:

$$\frac{d\eta_1}{dz} = -\rho_1 = \frac{\delta_2}{\delta_1} \frac{\sigma_0 \frac{d^2\sigma_0}{dz^2} - \left(\frac{d\sigma_0}{dz}\right)^2}{\sigma_0^2} \quad (\text{G.38})$$

As  $\sigma_0$  is finite for all  $z$ , this evaluates to zero where:

$$\sigma_0 \frac{d^2\sigma_0}{dz^2} - \left(\frac{d\sigma_0}{dz}\right)^2 = 0 \quad (\text{G.39})$$

and so, substituting appropriately:

$$\left(\alpha + \beta \operatorname{erf}\left(\frac{z\sqrt{\delta_1}}{2}\right)\right) \left(-\frac{2\beta}{\sqrt{\pi}} \delta_1^{\frac{3}{2}} z e^{-\frac{z^2\delta_1}{4}}\right) - 4\beta^2 \frac{\delta_1}{\pi} e^{-\frac{z^2\delta_1}{2}} = 0 \quad (\text{G.40})$$

which reduces algebraically to

$$\gamma + \operatorname{erf}\left(\frac{z\sqrt{\delta_1}}{2}\right) + \frac{2}{z\sqrt{\pi\delta_1}}e^{-\frac{z^2\delta_1}{4}} = 0 \quad (\text{G.41})$$

and substituting with  $s = z\sqrt{\delta_1}/2$  then gives:

$$\gamma + \operatorname{erf}(s) + \frac{e^{-s^2}}{s \cdot \sqrt{\pi}} = 0 \quad (\text{G.42})$$

$\gamma$  relates systematically to  $c_L^*$  as  $c_L^* = (\gamma - 1)/(\gamma + 1)$  and hence  $s(c_L^*)$  can be plotted. This is shown below (Figure 2).

The substitution of the identity Equation G.41 back into Equation G.35 yields the result:

$$\eta_1(z_{\text{LJP}}) = -s(\gamma) \cdot \frac{\delta_2}{\sqrt{\delta_1}} \quad (\text{G.43})$$

and hence

$$-\xi(X_{\text{LJP}}) \approx \frac{\delta_2 \cdot s(\gamma)}{\sqrt{\delta_1 \tau}} \quad (\text{G.44})$$

as plotted asymptotically in the main text.

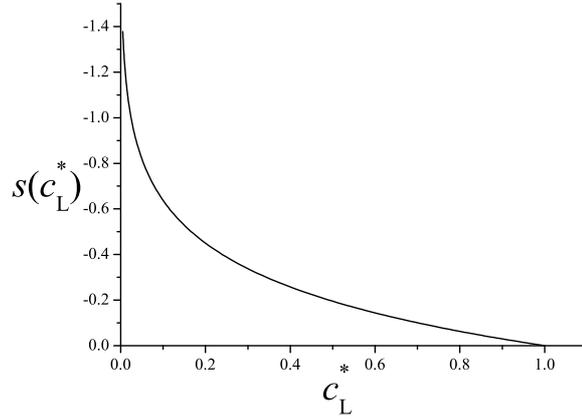


Figure 2: The ‘diffusion coefficient’  $s(\gamma)$  for the junction, plotted as  $s(c_L^*)$  where  $c_L^* = C_L^*/C_R^*$ .

## H $\tau \rightarrow \infty$ asymptotic analysis (Type 2)

The following is a brief summary of work by Hickman<sup>8</sup> on  $\tau \rightarrow \infty$  asymptotic analysis of the Type 2 case, followed by extended analysis of his results in the context of junction motion, and comparison with simulation.

In the general case of the Boltzmann transformed Nernst-Planck-Poisson equations for  $k$  arbitrary species, the concentrations  $c_k$ , and  $\eta$ , the dimensionless potential gradient, are functions  $f = f(z, u)$  which are assumed to take the form of a power series:

$$f(z, u) = \sum_{i=0}^{\infty} f_i(z) u^i \quad (\text{H.1})$$

So, generally:

$$D'_k \left( \sum_{i=0}^{\infty} \frac{d^2 c_{k,i}}{dz^2} u^i + z_k \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \frac{d}{dz} (c_{k,i} \eta_j) u^{i+j-1} \right) + \frac{z}{2} \sum_{i=0}^{\infty} \frac{dc_{k,i}}{dz} u^i + \sum_{i=0}^{\infty} i c_{k,i} u^i = 0 \quad (\text{H.2})$$

$$\sum_{i=0}^{\infty} \frac{d\eta_i}{dz} u^i + \sum_k z_k \sum_{i=0}^{\infty} c_{k,i} u^i = 0 \quad (\text{H.3})$$

From homogeneity we may collect terms in  $u^i$  from the equations, giving:

$$D'_k \left( \frac{d^2 c_{k,i}}{dz^2} + z_k \sum_{j=0}^{i+1} \frac{d}{dz} (c_{k,j} \eta_{i+1-j}) \right) + \frac{z}{2} \frac{dc_{k,i}}{dz} + i c_{k,i} = 0 \quad (\text{H.4})$$

$$\frac{d\eta_i}{dz} + \sum_k z_k c_{k,i} = 0 \quad (\text{H.5})$$

From the arguments in Supporting Information G,  $\eta_0$  must be zero, and therefore from terms in  $u^0$  (setting  $i = 0$  above) it follows that:

$$\sum_k z_k c_{k,0} \equiv \rho_0 = 0 \quad (\text{H.6})$$

$$D'_k \left( \frac{d^2 c_{k,0}}{dz^2} + z_k \frac{d}{dz} (c_{k,0} \eta_1) \right) + \frac{z}{2} \frac{dc_{k,0}}{dz} = 0 \quad (\text{H.7})$$

The first equation here is simply a statement of electroneutrality at infinite time. This invites us to take the sum of the Nernst-Planck equations, Equation H.7, multiplied by  $z_k$  in each case, as then one

term will be in  $\rho_0$  and can be removed. Hence:

$$\begin{aligned} \sum_k z_k D'_k \left( \frac{d^2 c_{k,0}}{dz^2} + z_k^2 \frac{d}{dz} (c_{k,0} \eta_1) \right) + \frac{z}{2} \frac{d\rho_0}{dz} &= \sum_k z_k D'_k \left( \frac{d^2 c_{k,0}}{dz^2} + z_k^2 \frac{d}{dz} (c_{k,0} \eta_1) \right) \\ &= 0 \end{aligned} \quad (\text{H.8})$$

Integrating between  $z$  and  $-\infty$ , where  $\eta_1 = dc_k/dz = 0$  from the boundary conditions, we find:

$$\sum_k z_k D'_k \frac{dc_{k,0}}{dz} + \sum_k z_k^2 D'_k (c_{k,0} \eta_1) = 0 \quad (\text{H.9})$$

which is a useful identity. The equations here are not directly solvable, however, without a further perturbation.

A perturbation of the following form is chosen. Let:

$$f_i(z) = \sum_{j=0}^{\infty} f_{ij}(z) \mu^j \quad (\text{H.10})$$

where

$$\mu = D'_{\max} - 1 \quad (\text{H.11})$$

Additionally the following shorthand is introduced:

$$\delta_k = \frac{D'_k - 1}{\mu} \quad \therefore \quad D'_k = \mu \delta_k + 1 \quad (\text{H.12})$$

Note that for example, in the NaCl—KCl case,  $\mu \approx 0.2$  and so only terms up to  $\mu^2$  ought need to be considered for close agreement. Unfortunately, all terms above  $\mu^0$  introduce special functions, such as  $s(\gamma)$  above, and so some numerical analysis is in fact required.

Substitution for  $D'_k$  in Equations H.7 and H.9 gives:

$$z_k D'_k \frac{d}{dz} (c_{k,0} \eta_1) + \mu \delta_k \frac{d^2 c_{k,0}}{dz^2} + \left( \frac{d^2 c_{k,0}}{dz^2} + \frac{z}{2} \frac{dc_{k,0}}{dz} \right) = 0 \quad (\text{H.13})$$

$$\sum_k z_k \mu \delta_k \frac{dc_{k,0}}{dz} + \sum_k z_k \frac{dc_{k,0}}{dz} + \sum_k z_k^2 D'_k (c_{k,0} \eta_1) = \sum_k z_k \delta_k \mu \frac{dc_{k,0}}{dz} + \sum_k z_k^2 D'_k (c_{k,0} \eta_1) = 0 \quad (\text{H.14})$$

in which the Nernst-Planck equation has now been separated into a general portion implying diffusion at a normalised  $D'_k = 1$  (the mean diffusive rate of the system) and a specific portion which has

$\mu$ -dependent component for the diffusive rate of the individual species ( $\delta_k$ ), and a perturbation arising from migration. The effect of an expansion in  $\mu$  is to neglect the diffusive part of this specific portion.

Now, substituting Equation H.10 into the above:

$$z_k D'_k \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \frac{d}{dz} (c_{k,0i} \eta_{1j}) \mu^{i+j} + \sum_{i=0}^{\infty} \delta_k \frac{d^2 c_{k,0i}}{dz^2} \mu^{i+1} + \sum_{i=0}^{\infty} \left( \frac{d^2 c_{k,0i}}{dz^2} + \frac{z}{2} \frac{dc_{k,0i}}{dz} \right) \mu^i = 0 \quad (\text{H.15})$$

$$\sum_k z_k \sum_{i=0}^{\infty} c_{k,0i} \mu^i = 0 \quad (\text{H.16})$$

$$\sum_k z_k \delta_k \sum_{i=0}^{\infty} \frac{dc_{k,0i}}{dz} \mu^{i+1} + \sum_k z_k^2 D'_k \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} (c_{k,0i} \eta_{1j}) \mu^{i+j} = 0 \quad (\text{H.17})$$

Collecting powers of  $\mu$ :

$$z_k D'_k \sum_{j=0}^i \frac{d}{dz} (c_{k,0j} \eta_{1(i-j)}) + \delta_k \frac{d^2 c_{k,0(i-1)}}{dz^2} + \left( \frac{d^2 c_{k,0i}}{dz^2} + \frac{z}{2} \frac{dc_{k,0i}}{dz} \right) = 0 \quad (\text{H.18})$$

$$\sum_k z_k c_{k,0i} = 0 \quad (\text{H.19})$$

$$\sum_k z_k \delta_k \frac{dc_{k,0(i-1)}}{dz} + \sum_k z_k^2 D'_k \sum_{j=0}^i (c_{k,0j} \eta_{1(i-j)}) = 0 \quad (\text{H.20})$$

and considering initially  $i = 0$  here, we have:

$$z_k D'_k \frac{d}{dz} (c_{k,00} \eta_{10}) + \left( \frac{d^2 c_{k,00}}{dz^2} + \frac{z}{2} \frac{dc_{k,00}}{dz} \right) = 0 \quad (\text{H.21})$$

$$\sum_k z_k c_{k,00} = 0 \quad (\text{H.22})$$

$$\sum_k z_k^2 D'_k (c_{k,00} \eta_{10}) = 0 \quad (\text{H.23})$$

From the latter it follows that  $\eta_{10} = 0$  and hence the following applies for all species:

$$\frac{d^2 c_{k,00}}{dz^2} + \frac{z}{2} \frac{dc_{k,00}}{dz} = 0 \quad (\text{H.24})$$

and the only difference in the functional form of the leading term of the concentration profiles arises from the differing boundary conditions. This has the following solution, on substitution of the boundary conditions:

$$c_{k,00} = \frac{c_{k,R}^* + c_{k,L}^*}{2} + \frac{c_{k,R}^* - c_{k,L}^*}{2} \operatorname{erf} \left( \frac{z}{2} \right) \quad (\text{H.25})$$

and so in the special case of Type 2:

$$c_{A,00} = \frac{1}{2} \left( 1 - \operatorname{erf} \left( \frac{z}{2} \right) \right) \quad (\text{H.26})$$

$$c_{B,00} = \frac{1}{2} \left( 1 + \operatorname{erf} \left( \frac{z}{2} \right) \right) \quad (\text{H.27})$$

$$c_{X,00} = 1 \quad (\text{H.28})$$

Now considering Equation H.17 at  $i = 1$ , to find the leading non-zero term in the field,  $\eta_{11}$ :

$$\sum_k z_k \delta_k \frac{dc_{k,00}}{dz} + \sum_k z_k^2 D'_k (c_{k,00} \eta_{11}) = 0 \quad (\text{H.29})$$

On rearrangement we note that:

$$\eta_{11} = - \frac{\sum_k z_k \delta_k \frac{dc_{k,00}}{dz}}{\sum_k z_k^2 D'_k c_{k,00}} \quad (\text{H.30})$$

and in the Type 2 case, on substitution for the forms of  $c_{k,00}$ :

$$\begin{aligned} \eta_{11} &= - \frac{\delta_B - \delta_A}{2} \frac{\frac{1}{\sqrt{\pi}} e^{-\frac{z^2}{4}}}{D'_X + \frac{D'_B + D'_A}{2} + \frac{D'_B - D'_A}{2} \operatorname{erf} \left( \frac{z}{2} \right)} \\ &= - \frac{\delta_B - \delta_A}{D'_B - D'_A} \frac{\frac{1}{\sqrt{\pi}} e^{-\frac{z^2}{4}}}{\frac{D'_A + D'_B + 2D'_X}{D'_B - D'_A} + \operatorname{erf} \left( \frac{z}{2} \right)} \\ &= - \frac{D'_B - D'_A}{D'_B - D'_A} \frac{1}{\mu} \frac{\frac{1}{\sqrt{\pi}} e^{-\frac{z^2}{4}}}{\gamma + \operatorname{erf} \left( \frac{z}{2} \right)} \\ &= - \frac{1}{\mu} \frac{\frac{1}{\sqrt{\pi}} e^{-\frac{z^2}{4}}}{\gamma + \operatorname{erf} \left( \frac{z}{2} \right)} \end{aligned} \quad (\text{H.31})$$

where

$$\gamma = \frac{D'_A + D'_B + 2D'_X}{D'_B - D'_A} \quad (\text{H.32})$$

so giving the electric field, to the first approximation, as:

$$\eta_1(z) \approx \eta_{11}(z) \mu = - \frac{\frac{1}{\sqrt{\pi}} e^{-\frac{z^2}{4}}}{\gamma + \operatorname{erf} \left( \frac{z}{2} \right)} \quad (\text{H.33})$$

and so

$$\frac{\partial \theta}{\partial X} \approx - \frac{2}{\sqrt{\pi \tau}} \frac{e^{-z^2}}{\gamma + \operatorname{erf}(z)} \quad (\text{H.34})$$

A comparison of the electric field predicted by the Hickman theory with dynamic simulation is considered here for the first time (Figure 1). Evidently the agreement is not strong.

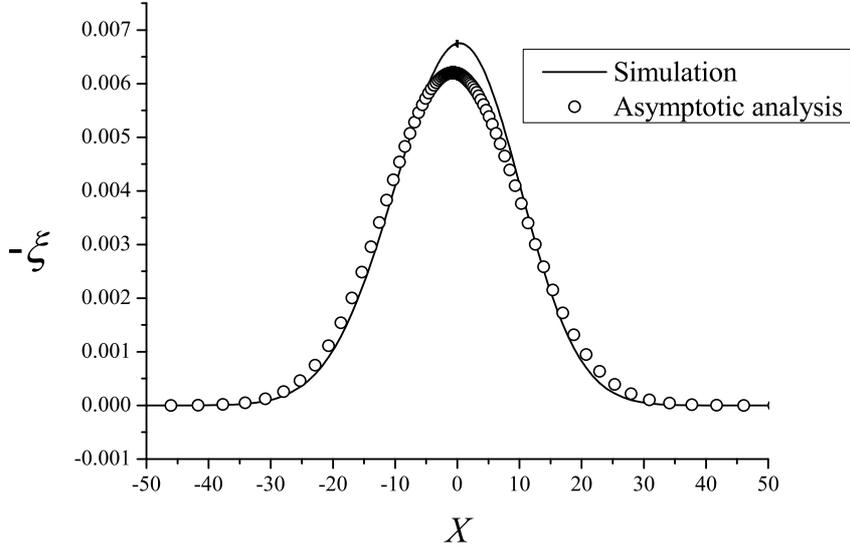


Figure 1: Comparison of the simulated electric field for the model NaCl—KCl (aq) system,  $-\xi$ , at long time ( $\tau = 100\tau_{\text{trs}}$ ) with the leading non-zero term,  $-\xi_{11}$ , in the asymptotic analysis introduced by Hickman.

Integrating the field (Equation H.33) from  $\infty$  to  $-\infty$  gives the liquid junction potential as:

$$\begin{aligned} \Delta\theta_{\text{LJP}} &= \int_{-\infty}^{\infty} \eta_{11}(z) \mu dz = [-\ln |\gamma + \text{erf}(z/2)|]_{-\infty}^{\infty} \\ &= \ln \left| \frac{\gamma - 1}{\gamma + 1} \right| \end{aligned} \quad (\text{H.35})$$

which on substitution of  $\gamma$  is simply the Type 2 Henderson equation (Equation 1.4, main text). Given the second perturbation required to achieve this, of which only the leading term was considered, the Henderson equation is therefore not exact for Type 2, even as  $\tau \rightarrow \infty$ . For more than two species, the Henderson equation is the leading non-zero term of an expansion of the  $\tau \rightarrow \infty$  asymptote in powers of  $\mu$ , which represents the range of diffusion coefficients of the system. It is accurate only

where the diffusion coefficients of all species are similar, i.e. as  $\Delta\theta_{LJP} \rightarrow 0$ ; otherwise a correction to the Henderson equation must arise.

## I Trends in $\Delta X_\theta$ in the Type 2 case

A study of the dynamic trends in  $\Delta X_\theta$  for the Type 2 example NaCl—KCl (aq) show identical trends to the Type 1 case. The same definition as in Section 3.2.6 is used.

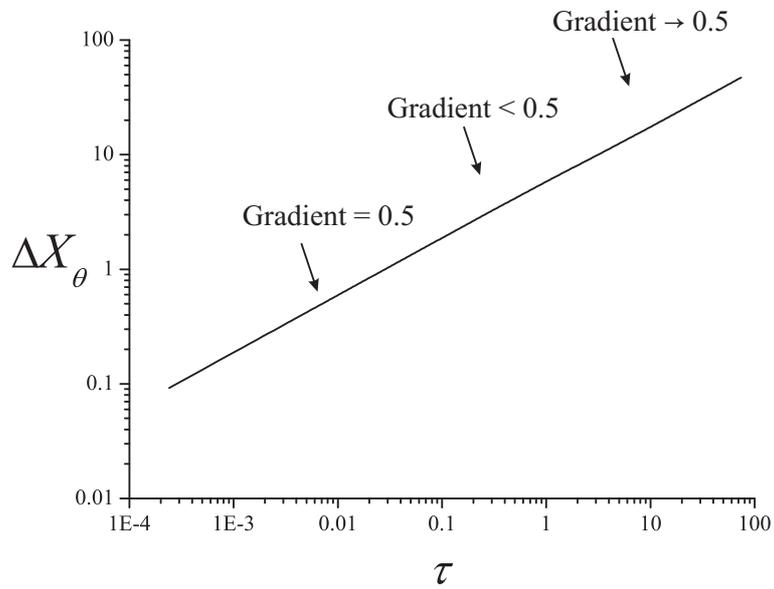


Figure 1:  $\Delta X_\theta$  as a function of  $\tau$  on a logarithmic scale, for the model Type 2 NaCl—KCl system.

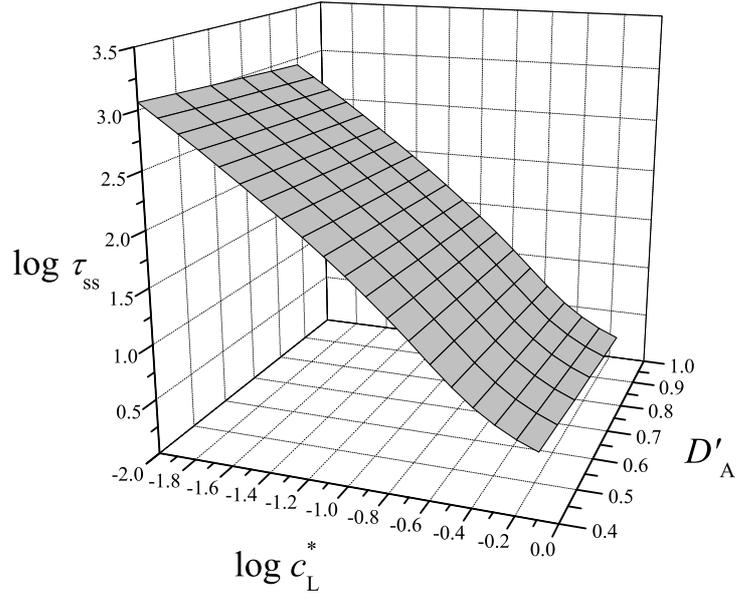


Figure 1: Comparison of  $\tau_{ss}$ , on a logarithmic scale, required to achieve asymptotic behaviour for a Type 1 system with varying  $D'_A$  and  $c_L^*$ .

## J Trends in the temporal and spatial extents of liquid junctions

The following plots are those referred to in the discussions in Sections 3.3 and 3.5 in the main text, concerning the temporal and spatial extents of liquid junctions.

The variables  $\tau_{ss}$  and  $\Delta X_{\theta,ss}$ , defined:

$$\tau_{ss} = \tau(\Delta\phi_{LJP} = 0.99\Delta\phi_{Henderson}) \quad (J.1)$$

$$\Delta X_{\theta,ss} = \Delta X_{\theta}(\tau = \tau_{ss}) \quad (J.2)$$

are plotted as functions of  $c_L^*$  and  $D'_A$  in the Type 1 case, and as functions of  $D'_A$  and  $D'_B$  in the Type 2 case. For the Type 1 case, dimensional plots for the HCl system are also shown.

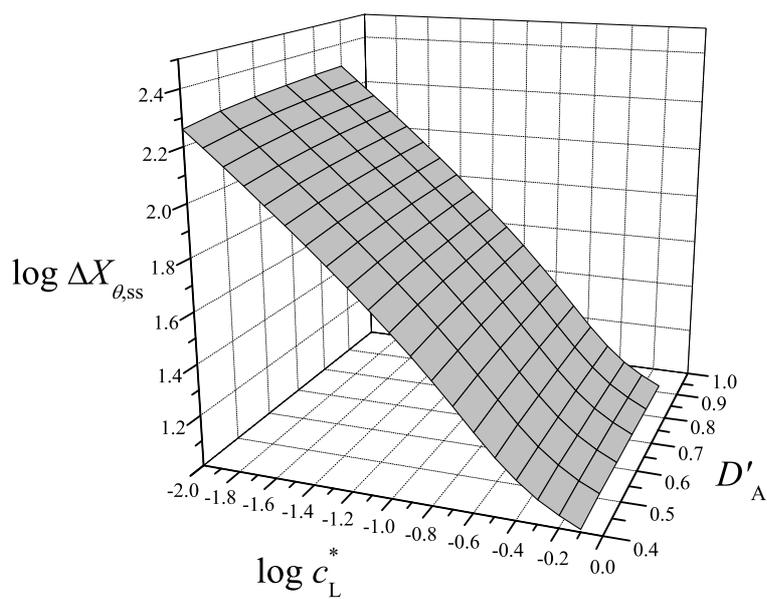


Figure 2: Comparison of  $\Delta X_{\theta,ss}$ , on a logarithmic scale, at  $\tau_{ss}$  for a Type 1 system with varying  $D'_A$  and  $c_L^*$ .

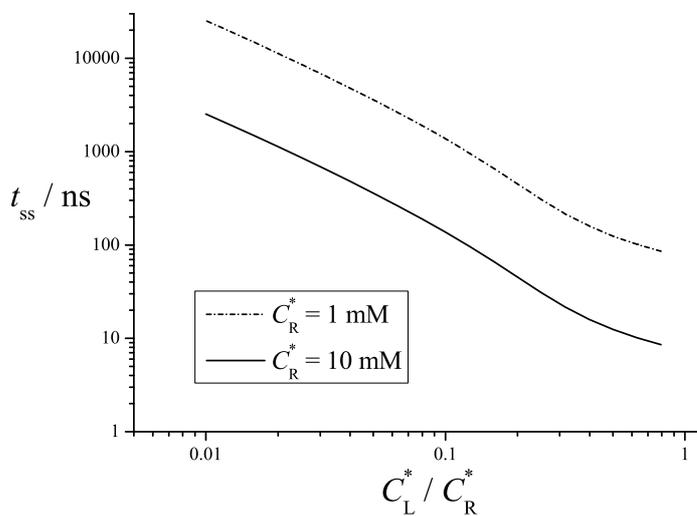


Figure 3: Comparison of  $t_{ss}$ , on a logarithmic scale, required to achieve asymptotic behaviour for the model Type 1 HCl (aq) system at two values of  $C_R^*$  and varying concentration ratios  $C_L^*/C_R^*$ .

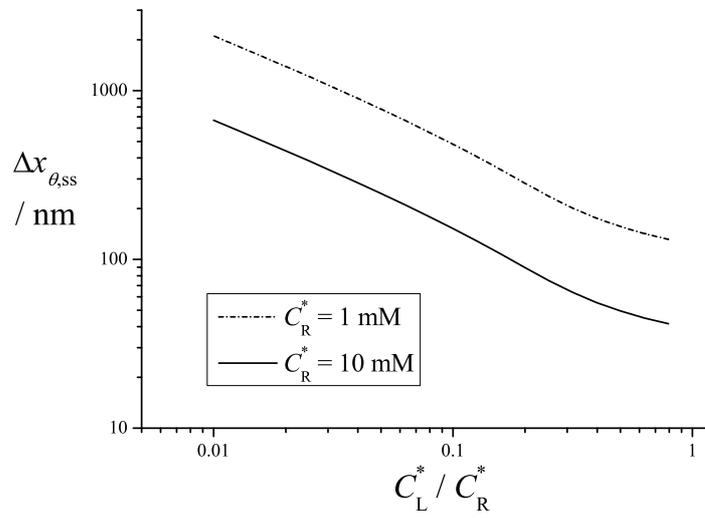


Figure 4: Comparison of  $\Delta x_{\theta}$ , on a logarithmic scale, at  $t_{ss}$  for the model Type 1 HCl (aq) system at two values of  $C_R^*$  and varying concentration ratios  $C_L^*/C_R^*$ .

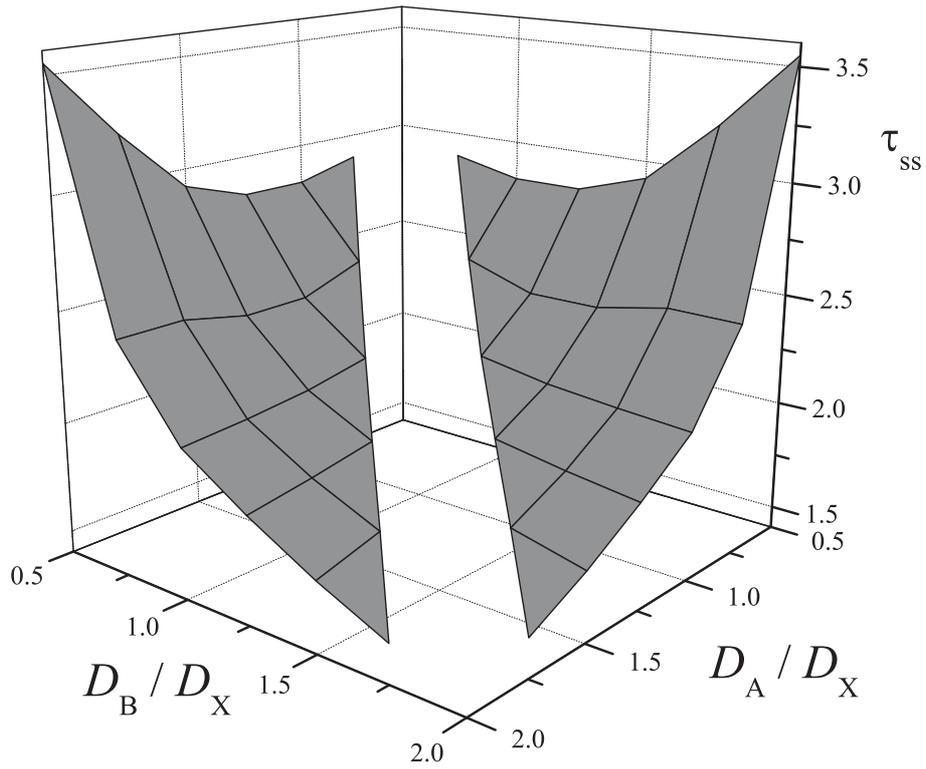


Figure 5: Comparison of  $\tau_{ss}$  required to achieve asymptotic behaviour for a Type 2 system with varying  $D'_A$  and  $D'_B$ . The absent central region is where  $D'_A = D'_B$  and hence no liquid junction potential exists.

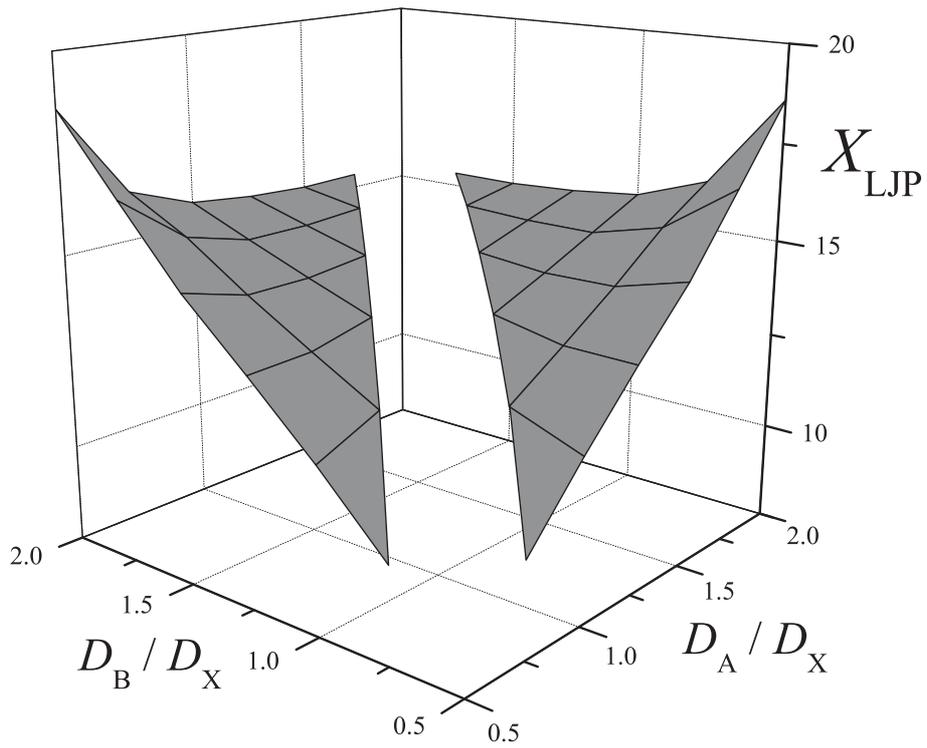


Figure 6: Comparison of  $\Delta X_{\theta,ss}$  at  $\tau_{ss}$  for a Type 2 system with varying  $D'_A$  and  $D'_B$ . The absent central region is where  $D'_A = D'_B$  and hence no liquid junction potential exists.

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