Non-Faradaic electric currents in the Nernst-Planck equations and ‘action at a distance’ diffusiophoresis in crossed salt gradients

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In the Nernst-Planck equations in two or more dimensions, a non-Faradaic electric current can arise as a consequence of connecting patches with different liquid junction potentials. Whereas this current vanishes for binary electrolytes or one-dimensional problems, it is in general non-vanishing for example in crossed salt gradients. For a suspended colloidal particle, electrophoresis in the corresponding electrostatic potential gradient is generally vectorially misaligned with chemiphoresis in the concentration gradients, and diffusiophoresis (via electrophoresis) can occur in regions where there are no local concentration gradients (‘action at a distance’). These phenomena may provide new opportunities to manipulate and sort particles, in microfluidics devices for example.

The growing realisation that diffusiophoresis is a potent and ubiquitous non-equilibrium transport mechanism for micron-sized colloidal particles has led to a recent surge of interest in the phenomenon [1–10]. For example, diffusiophoresis is effective at injecting or ousting particles from dead-end channels [11,12], has been identified as a hitherto unsuspected pore-scale particulate soil removal process in laundry detergency [13], implicated as a new opportunities to manipulate and sort particles, in microfluidic devices, and may additionally arise if bulk flows are driven by diffusion and drift in the electric field. For simplicity I omit advection terms although these are certainly relevant in microfluidics devices, and may additionally arise if bulk flows are driven by diffusio-osmotic effects [12].

The Nernst-Planck equations must be augmented by a closure for the electrostatic potential. At a fundamental level this is the Poisson equation, $\nabla^2 \phi = -\epsilon \rho_s$, where $\rho_s = \sum_i z_i \rho_i$ is the space charge (in units of $\epsilon$) and $\epsilon$ is the permittivity (assumed constant) of the supporting medium. The combined set are then known as the Poisson-Nernst-Planck (PNP) equations.

Let me start with the Nernst-Planck equations which govern ion transport in these problems [22,23],

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \mathbf{J}_i = 0 , \quad \mathbf{J}_i = -D_i(\nabla \rho_i + \rho_i z_i \nabla \phi) . \quad (1)$$

In these, $\rho_i$ is the density of the i-th ionic species, $D_i$ is the corresponding diffusion coefficient, $z_i$ the charge on the ion in units of $\epsilon$, where $\epsilon$ is the unit of elementary charge, and $\phi = \epsilon \phi/k_B T$ is a dimensionless electrostatic potential wherein $k_B T$ is the unit of thermal energy and $\phi$ is the actual electrostatic potential. Eqs. (1) combine mass conservation laws for the individual ion densities with expressions for the fluxes driven by diffusion and drift in the electric field. For simplicity I omit advection terms although these are certainly relevant in microfluidics devices, and may additionally arise if bulk flows are driven by diffusio-osmotic effects [12].

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Crucially, local charge neutrality does not necessarily imply a vanishing electric current $\mathbf{I} = \sum_i z_i \mathbf{J}_i$ (in units of $e$) in the outer domain. Rather, by summing the mass conservation laws in Eqs. (1) one can only conclude that the current should be solenoidal ($\nabla \cdot \mathbf{I} = 0$). In fact, even





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for pure diffusion problems without Faradaic reactions \[31\], a non-vanishing current \( I \neq 0 \) is not only possible but may be mandatory. To see this, insert the fluxes \( J_i \) from Eqs. \[1\] into the definition of \( I \) to obtain

\[
I = -\nabla g + \sigma \mathbf{E}.
\]

(2)

This decomposes \( I \) into the sum of a diffusion current, and a conduction current obeying Ohm’s law \[23\]. In this \( g = \sum_i z_i D_i \rho_i \) is a weighted sum of ion densities, \( \sigma = \sum_i z_i^2 D_i \rho_i \) is the conductivity, and \( \mathbf{E} = -\nabla \varphi \) is the electric field (the latter two are in semi-reduced units). Proceeding from Eq. \[2\], if \( I = 0 \) then it is easy to show \( \nabla \times \mathbf{E} = \sigma^{-2} \nabla \sigma \times \nabla g \). But there is no particular reason why the cross product on the right hand side should vanish, even though \( \nabla \times \mathbf{E} = 0 \) because \( \mathbf{E} = -\nabla \varphi \). Thus we are forced to conclude that in general \( I \neq 0 \). As another way to see this, by taking the curl of Eq. \[2\] one can eliminate the electrostatic potential to find

\[
\sigma \nabla \times \mathbf{I} = \nabla \sigma \times (\mathbf{I} + \nabla g).
\]

(3)

This is an inhomogeneous partial differential equation for \( \mathbf{I} \), and again supports the notion that \( I \neq 0 \) is driven by crossed gradients in the form \( \nabla \sigma \times \nabla g \neq 0 \).

Of course there are many examples where \( I \) does vanish. One such case is where the gradients are one-dimensional so that \( \varphi \) can be found by quadrature \[19\]. Another important case is that of a b\textit{inary} electrolyte \[22, 23\] for which \( \varphi = -\beta \ln(\rho) \) (the diffusion or \textit{liquid junction potential}). Here \( \beta = (D_1 - D_2)/(q_1 D_1 + q_2 D_2) \) is a normalised diffusivity contrast, and I suppose that \( z_1 > 0 \) and \( z_2 < 0 \), set \( q_i = |z_i| \), and use \( \rho_i = \rho_1/\rho_2 \) for the overall electrolyte concentration \[33\].

The simplest situation where an electric current \textit{does} arise is where there are three ion species, with crossed gradients. To explore this, suppose there are two cations with a common anion. Let the respective ion densities be \( \rho_1, \rho_2 \) and \( \rho_0 \), with corresponding diffusivities \( D_1, D_2 \) and \( D_0 \), and let the ions be univalent (\( |z_i| = 1 \)). For local charge neutrality we have \( \rho_0 = \rho_1 + \rho_2 \). Then \( \nabla \sigma \times \nabla g = 2D_0(D_2 - D_1)\nabla \rho_1 \times \nabla \rho_2 \). This suggests that the appearance of an electric current requires crossed gradients \textit{and} contrasting cation diffusivities (\( D_1 \neq D_2 \)), but no particular requirement is placed on the anion diffusivity. Thus one of the gradients can be in a supporting electrolyte (\textit{i.e.} \( \beta \approx 0 \)), as in the example below.

To summarise the mathematical problem thus far, given \( g \) and \( \sigma \) and supposing that \( \mathbf{I} \cdot \mathbf{n} \) is specified on the boundaries of the domain of interest, we must find the current distribution that satisfies Eq. \[3\] with \( \nabla \cdot \mathbf{I} = 0 \) and \( \mathbf{E} = -\nabla \varphi \). To prove solutions do exist, and are unique, we can note that this combination implies \[23, 34\]

\[
\nabla \cdot (\sigma \nabla \varphi) + \nabla^2 g = 0.
\]

(4)

This is an inhomogeneous Poisson equation for \( \varphi \) with the equivalent of a spatially-varying dielectric permittivity. Existence and uniqueness of \( \varphi \) (up to an additive constant) then follows by analogy with standard

![FIG. 1. Crossed salt gradients at \( t = 0 \), between HCl (horizontal) and KBr (vertical) \[32\]: (a) electrostatic potential (equipotential lines labelled in mV) and space charge (colored background); (b) circulating electric current (colored by magnitude); (c) equivalent circuit with HCl gradients labelled by liquid junction potentials (in brackets are the ‘open circuit’ values calculated from \( \Delta \varphi = -\beta \ln(\sigma_2/\sigma_1) \) where \( \sigma_2/\sigma_1 \) is the ratio of conductivities across the junction \[33\]); (d) magnitude of current along the \( x = y \) diagonal (the dotted line is \( 1/r \sim 1/|x - x_0| \) where \( x_0 = 40 \mu m \)).]
with a 100-fold gradient in an electrolyte with a large diffusivity contrast (HCl, $\beta = 0.64$), crossed with a 100-fold gradient in a supporting electrolyte (KBr, $\beta = -0.01$) \cite{27}. The concentration gradients are initially localised to the mid-planes, with widths 10 $\mu$m \cite{22}, so that the square domain is divided into four quadrants as shown in Fig. 1a. The actual concentration units need not be specified since the overall units of concentration can be factored out of the Nernst-Planck equations. For this demonstration I choose a problem with four rather than three ions, since this maintains the distinction between the two electrolytes.

I solve Eq. (4) in this square domain, with $\mathbf{I} \cdot \mathbf{n} = 0$ on the boundaries. For details see Appendix B. Fig. 1a shows that there is a significant liquid junction potential ($\Delta \phi \approx 62$ mV) between the two lower quadrants, corresponding approximately to the expected value for HCl treated as a binary electrolyte. The junction potential between the upper two quadrants is much weaker though ($\Delta \phi \approx 25$ mV), as might be expected for HCl in the presence of a supporting electrolyte \cite{33}. It is essentially this difference that drives the circulating electric current (Fig. 1b). By joining the upper and lower halves, it is as if we have short-circuited the two liquid junctions, as sketched in Fig. 1c. The resulting current is distributed throughout the square domain, as befits the minimum Ohmic heating principle. Crucially, in the lower-left quadrant where the conductivity is small, this generates a significant electric field throughout this region as indicated by the equipotential lines in Fig. 1a. Also shown in Fig. 1a is the space charge from $\rho_z = - (\varepsilon k_B T / e^2) \nabla^2 \phi$. Note that $|\rho_z| \lesssim 10^{-8} \text{M}$ so that local charge neutrality should normally be a very good approximation \cite{38}. Finally, Eq. (3) implies $\mathbf{I}$ should be irrotational as well as solenoidal, in regions where the gradients vanish. This explains why approximately $|\mathbf{I}| \approx 1/r$ in the lower left quadrant (Fig. 1a), and why the equipotential lines are approximately radial in this quadrant (Fig. 1b).

As time progresses, the gradients in this confined system dissipate by coupled diffusion. To track the evolving concentration fields, I solve the Nernst-Planck equations with boundary conditions $\mathbf{J} \cdot \mathbf{n} = 0$, computing the electrostatic potential from Eq. (4) at each step \cite{39}. Fig. 2 shows the situation after 250 ms. In the upper half space the more mobile $\text{H}^+$ has spread out much further than the less mobile $\text{Cl}^-$ (Fig. 2a), since with the high concentration of KBr in this region the ion densities become decoupled. Additionally the circulating current corresponds to cations moving clockwise and anions moving anticlockwise, which distorts the ion density profiles, as seen for $\text{K}^+$ and $\text{Br}^-$ (Fig. 2b).

What are the implications for diffusiophoresis of a suspended colloidal particle? Obviously, this depends on where the particle is located as well as its zeta potential. Here I predict trajectories by integrating $d\mathbf{R} / dt = \mathbf{U}$, where the diffusiophoretic drift velocity is \cite{5,16,20,40}

$$
\mathbf{U} = \frac{\varepsilon}{\eta} \left( \frac{k_B T}{e} \right)^2 \left[ 4 \ln \cosh \left( \frac{\xi}{4} \right) \nabla \ln \rho - \xi \nabla \varphi \right] \quad (5)
$$
FIG. 3. Diffusiophoresis: trajectories of colloid particles with different zeta potentials (labels) starting from (a) the centre of the crossed gradients, and (b) a location in the lower left quadrant. Starting points are marked by a cross, and positions at \( t = 500 \text{ ms} \) by filled circles.

(see also Appendix [B]). In this \( \rho = \sum_i \rho_i \) is the total ion density, \( \eta \) is the viscosity of the medium, and \( \bar{\zeta} = e\zeta/k_BT \) is the non-dimensionalised zeta potential. The two terms in Eq. (5) correspond respectively to chemiphoresis in the overall concentration gradient, and electrophoresis in the electrostatic potential gradient.

Sample trajectories are shown in Fig. 3. In the lower-left quadrant (Fig. 3a) the electric field corresponding to the gradient in \( \phi \) drives diffusiophoresis via electrophoresis even though there are initially no local concentration gradients. I term this unusual phenomenon diffusiophoretic ‘action at a distance’. Since the electric field also drives the electric current, in this quadrant the current density \( \mathbf{J} \) is initially parallel to \( \mathbf{E} \); this explains the initial coincidence of the trajectories. In contrast, for a particle which finds itself in the middle of the crossed salt gradients (Fig. 3b), electrophoresis and chemophoresis are vectorially misaligned even initially, so that particles with different zeta potentials are propelled along diverging trajectories even if they have the same sign of charge.

The design of devices which exploit these striking effects is a clearly a promising avenue for future work. I note that in this situation one loses the logarithmic sensitivity exhibited in binary electrolytes [2][13][11], so that the distance over which particles move is limited by the relaxation time for the ion densities. This can be alleviated by using soluto-inertial beacons [6][21], or microfluidic devices in which long-lived gradients can be established [11][5][9].

To summarise, a rich phenomenology arises in the Nernst-Planck equations when considering multicomponent electrolytes in more than one dimension. In particular, circulating (solenoidal) electric currents appear when patches with different liquid junction potentials are connected by the intervening electrolyte solution. The electric fields associated with these currents can drive ‘action at a distance’ diffusiophoresis of suspended colloidal particles, even in the absence of local concentration gradients. This is a definitive prediction of the Nernst-Planck equations, combined with the current understanding of diffusiophoresis of charged colloidal particles, and it would be fascinating to put to an experimental test.

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Appendix A: Uniqueness

Here I provide a direct proof of uniqueness of \( \phi \) in Eq. (4). Suppose there are two solution pairs \( (\mathbf{I}_1, \phi_1) \) and \( (\mathbf{I}_2, \phi_2) \), such that \( \mathbf{I}_1 \cdot \mathbf{n} = \mathbf{I}_2 \cdot \mathbf{n} \) on some domain boundary with vector normal \( \mathbf{n} \). Subtracting the corresponding versions of Eq. (2) yields a homogeneous problem in which the difference solution, with \( \mathbf{I} = \mathbf{I}_2 - \mathbf{I}_1 \) and \( \phi = \phi_2 - \phi_1 \), satisfies Ohm’s law \( \mathbf{I} = \sigma \mathbf{E} \) where \( \mathbf{I} \cdot \mathbf{n} = 0 \) on the domain boundary, \( \nabla \cdot \mathbf{E} = 0 \) in the interior, and \( \mathbf{E} = -\nabla \phi \). Now consider

\[
\nabla \cdot (\mathbf{E} \mathbf{I}) = \mathbf{I} \cdot \nabla \nabla \phi. \tag{A1}
\]

The first term on the right hand side vanishes as a consequence of the solenoidal nature of \( \mathbf{I} \), and the second term simplifies to \( \mathbf{I} \cdot \nabla \phi = -\sigma \mathbf{E}^2 \). Integrate Eq. (A1) over the domain of interest and use the divergence theorem to get

\[
\int \nabla \cdot (\mathbf{E} \mathbf{I}) \, dV = \int \mathbf{I} \cdot \mathbf{n} \, dS = 0 \tag{A2}
\]

(because \( \mathbf{I} \cdot \mathbf{n} = 0 \) on the boundary). We conclude that

\[
\int \sigma \mathbf{E}^2 \, dV = 0. \tag{A3}
\]

But \( \sigma > 0 \) and \( \mathbf{E}^2 \geq 0 \), so this implies \( \mathbf{E} = 0 \) everywhere, and hence \( \mathbf{I} = 0 \) and \( \phi = \text{constant} \). This is the desired result. It means that the solution pairs \( (\mathbf{I}_1, \phi_1) \) and \( (\mathbf{I}_2, \phi_2) \) in the original inhomogeneous problem can at most differ by a constant in \( \phi \).

Appendix B: Variational principle

An inhomogeneous Poisson equation such as that given in Eq. (4) has an equivalent variational principle. In the
bookkeeping, with the convergence criterion being that the relative change in \( \phi \) in subsequent iterations falls to less than \( 10^{-14} \). For boundary conditions I set the fluxes to zero on the exterior edges. Note that the actual space charge is not represented as such in the calculation, and deviations from \( \nabla \cdot \mathbf{I} = 0 \) are numerical errors.

To solve the time-dependent Nernst-Planck equations, I use a standard forward-time centered-space (FTCS) scheme \([36]\) based on the above grid decomposition, with a time step \( \delta t = 0.025 \text{ ms} \times (h/\mu m)^2 \), which comfortably satisfies the usual Courant-Friedrichs-Lewy condition since the maximum diffusion coefficient is \( D = 9.31 \mu m^2 \text{ms}^{-1} \) (for \( H^+ \)) so \( D \delta t/h^2 < 0.5 \).

To compute the trajectories of particles undergoing diffusiophoresis I integrate the kinematic equations in Eq. \((5)\) using a simple first order forward Euler scheme with \( \Delta t = 5 \text{ ms} \) (a multiple of \( \delta t \)), and bivariate interpolation (on the same grid as above) to calculate off-lattice approximations to \( \nabla \ln \rho \) and \( \nabla \phi \).

Fig. 4 shows that the computed trajectories depend very little on the underlying grid spacing and consequent choices for time step. I only show the \( h \)-dependence for trajectories of particles starting in the lower left quadrant; the trajectories of particles which start in the centre of the crossed gradients show even smaller \( h \)-dependence. All calculations reported in the main text are for \( h = 1 \mu m \) (100\(^2\) grid).

Appendix D: Diffusiophoretic drift coefficients

Diffusiophoresis in multicomponent electrolytes has been considered by several groups recently \([5, 18, 20]\). Assuming a thin EDL, it is convenient to start with a general expression for the diffusiophoretic drift of a suspended colloidal particle arising from bulk chemical potential gradients,

\[
\mathbf{U} = \sum_i \mathcal{M}_i \nabla \mu_i. \tag{D1}
\]

Restricting the analysis to the tractable but practically relevant case of monovalent electrolytes, the mobilities are \( \mathcal{M}_i = (\rho_i/\rho) \times \mathcal{M}_\pm \) where \( \mathcal{M}_\pm = \frac{e k_B T}{\eta c^2} \left[ 4 \ln \cosh \frac{e \zeta}{k_B T} \pm \frac{e \zeta}{k_B T} \right] \tag{D2} \)

according to the sign of the ion \( (z_i = \pm 1) \). Here \( \rho = \sum_i \rho_i \) as in the main text, \( \eta \) is viscosity, and \( \zeta \) is the particle zeta potential. This formalism extends to include electrophoresis if one employs the electrophoretic potentials,

\[
\mu_i = k_B T \ln \rho_i + e z_i \phi. \tag{D3}
\]

Combining Eqs. \((D1)\) and \((D2)\), cross terms cancel since \( \sum_i z_i \rho_i = 0 \), yielding Eq. \((5)\) used in the main text. Note that the second term in Eq. \((5)\) simplifies to the well-known Helmholtz-Smoluchowski result \(- (e \zeta/\eta) \nabla \phi \tag{10}\).
[1] B. Abécassis, C. Cottin-Bizonne, C. Ybert, A. Ajdari, and L. Bocquet, Nat. Mater. 7, 785 (2008).
[2] J. Palacci, C. Cottin-Bizonne, C. Ybert, and L. Bocquet, Soft Matter 8, 980 (2012).
[3] A. Reinmüller, H. J. Schöpe, and T. Palberg, Langmuir 29, 1738 (2013).
[4] D. Florea, S. Musa, J. M. Huyghe, and H. M. Wyss, Proc. Natl. Acad. Sci. USA 111, 6554 (2014).
[5] N. Shi, R. Nery-Azevedo, A. I. Abdel-Fattah, and T. M. Squires, Phys. Rev. Lett. 117, 258001 (2016).
[6] A. Banerjee, T. Williams, R. N. Azevedo, M. E. Helgeson, and T. M. Squires, Proc. Natl. Acad. Sci. USA 113, 8612 (2016).
[7] H. J. Keh, Curr. Opin. Colloid In. 24, 13 (2016).
[8] D. Velegol, A. Garg, R. Guha, A. Kara, and M. Kumara, Soft Matter 12, 4686 (2016).
[9] S. Shin, O. Shardt, P. B. Warren, and H. A. Stone, Nat. Commun. 8, 15181 (2017).
[10] S. Shin, J. T. Ault, P. B. Warren, and H. A. Stone, Phys. Rev. X 7, 041038 (2017).
[11] A. Kar, T.-Y. Chiang, I. O. Rivera, A. Sen, and D. Velegol, ACS Nano 9, 746 (2015).
[12] S. Shin, E. Um, B. Sabass, J. T. Ault, M. Rahimi, P. B. Warren, and H. A. Stone, Proc. Natl. Acad. Sci. USA 113, 257 (2016).
[13] S. Shin, P. B. Warren, and H. A. Stone, Phys. Rev. Appl. 9, 034012 (2018).
[14] R. P. Sear, Phys. Rev. Lett. 122, 128101 (2019).
[15] S. Shin, J. T. Ault, J. Feng, P. B. Warren, and H. A. Stone, Adv. Mater. 29, 1701516 (2017).
[16] J. L. Anderson, Annu. Rev. Fluid Mech. 21, 61 (1989).
[17] A. Brown and W. Poon, Soft Matter 10, 4016 (2014).
[18] T.-Y. Chiang and D. Velegol, J. Colloid Interf. Sci. 424, 120 (2014).
[19] A. Gupta, S. Shim, L. Issah, C. McKenzie, and H. A. Stone, Soft Matter, 10.1039/C9SM01780A (2019).
[20] A. Gupta, B. Rallabandi, and H. A. Stone, Phys. Rev. Fluids 4, 043702 (2019).
[21] A. Banerjee and T. M. Squires, Sci. Adv. 5, eaax1893 (2019).
[22] V. G. Levich, Physicochemical Hydrodynamics (Prentice-Hall, Englewood Cliffs, NJ, 1962).
[23] J. Newman and K. E. Thomas-Alvey, Electrochemical Systems (John Wiley & Sons, Hoboken, NJ, 2004).
[24] D. R. Hafemann, J. Phys. Chem. 69, 4226 (1965).
[25] H. J. Hickman, Chem. Eng. Sci. 25, 381 (1970).
[26] J. L. Jackson, J. Phys. Chem. 78, 2060 (1974).
[27] V. M. Aguilera, S. Mafé, and J. Pellicer, Electrochim. Acta 32, 483 (1987).
[28] M. Z. Bazant, K. Thornton, and A. Ajdari, Phys. Rev. E 70, 021506 (2004).
[29] M. Janssen and M. Bier, Phys. Rev. E 97, 052616 (2018).
[30] The value of ϕ where the outer solution meets the EDLs cannot be pre-determined, and indeed it is the mismatch between this and the true wall boundary condition that gives rise to an EDL in the first place.
[31] Technically I also assume small Dukhin number so that surface conduction in the EDLs can be neglected.
[32] The specific functional form is $c = c_0 + (c_1 - c_0) \text{erf}(x/w)$ where $c_0 = 0.01$ and $c_1 = 1$ are the limiting concentrations in arbitrary units, $x$ is the distance from the mid-plane, and $w = 10\mu m$ is the width.
[33] The binary electrolye case can be solved because the individual ion densities are slaved to each other by local charge neutrality so that $\nu = \nu_1 = \nu_2$ and $\sigma = \sigma_1 = \sigma_2$. Hence $\nu = \nu_1$ and $\nu_2$ can be integrated to determine $\nu_1$ up to a constant. A binary electrolye with a uniform background can also be solved, since in that case also $\nabla \nu = \beta \nabla \sigma$ and therefore $\nabla \nu = -\beta \ln \sigma$. This demonstrates that a background electrolyte reduces the diffusion potential, since it reduces the conductivity contrast; however the specific situation is transient since the electrostatic coupling in the Nernst-Planck equations will soon lead to all ion densities becoming non-uniform.
[34] R. A. Rica and M. Z. Bazant, Phys. Fluids 22, 112109 (2010).
[35] C. A. Coulson, Electricity (Oliver and Boyd, Edinburgh, 1961).
[36] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, Numerical Recipes, 3rd ed. (CUP, New York, 2007).
[37] The diffusivities of $H^+$, $Cl^-$, $K^+$, and $Br^-$ are 9.31, 2.03, 1.96, and $2.01 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$ respectively, taken from a database in the PHREEQC software package; see D. L. Parkhurst and C. A. J. Appelo, Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations (Tech. Rep. (U.S. Geol. Survey, Reston, VA, 2013).
[38] Interestingly the choice of units for the ion densities does not affect the calculation of the space charge $\rho_s$.
[39] The ion densities relax on a time scale $O(L^2/D) \sim 10$ s since $L = 100 \mu m$ and $D = 10^{-9} \text{ m}^2 \text{s}^{-1}$. On the other hand, the time scale for the electrostatic potential $\varphi$ and electric current $I$ to relax is $O(\lambda_D^2/D)$ as an RC circuit, the relevant capacitance is $O(\lambda_D/L)$ smaller than in the EDL charging problem. Then $L \gg \lambda_D$ implies $\varphi$ and $I$ are slaved to the ion densities. Further investigation of this aspect is left to future work.
[40] Eq. (5) assumes the ions are univalent.
[41] Logarithmic sensitivity in binary electrolytes follows by inserting $\rho = 2\rho_s$ and $\varphi = -\beta \ln \rho_s$ into Eq. (5), whereupon both terms acquire the same dependence on $\nabla \ln \rho_s$. 