Desalination shocks in microstructures

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The transport of ions in bulk electrolytes is governed by diffusion and convection, but the proximity of a charged surface introduces interfacial effects, such as electro-osmotic flow and surface conduction. In this paper, we describe a class of nonlinear electrokinetic phenomena that results from the competition between bulk and interfacial transport in microstructures. Mani, Zangle and Santiago recently showed that sharp concentration gradients can propagate away from a microchannel/nanochannel junction, analogous to shock waves in gases. Here, we elucidate the basic physics of “desalination shocks” and develop a theory of shock existence and propagation in complex microstructures. The crucial dimensionless parameter in our theory is the ratio of volume averaged surface charge to bulk countercharge, which controls the importance of surface conduction. Via similarity solutions and asymptotic analysis, we predict that desalination shocks accelerate and sharpen in narrowing channels and decelerate and weaken – or even disappear – in widening channels. Using volume-averaged transport equations for slowly varying microstructures, we predict that stable desalination shocks can also propagate in porous media. We conclude by discussing possible applications in microfluidic and electrochemical systems.

Introduction

Many electrochemical processes, such as electrodeposition, electrodialysis, and battery discharge, produce large salt concentration gradients in unsupported electrolytes [1]. In desalination, this is in fact the goal (to remove salt from water). In other situations, salt depletion is often undesirable, since it reduces electrochemical reaction kinetics and thus increases the over-potential required to maintain a desired current.

In the classical theory of electrochemical systems, it is generally assumed that salt concentration gradients advance into the bulk electrolyte by linear diffusion. This hypothesis provides the theoretical basis for many important experimental techniques, such as electrochemical impedance spectroscopy [2], cyclic or pulsed voltammetry [3], and intermitent titration methods [4]. In a concentrated electrolyte, ionic diffusion can be nonlinear (with a concentration-dependent diffusivity [1]), but the familiar square-root of time scaling of linear diffusion usually remains [5].

Recent experiments in microfluidics have shown that rather complicated, nonlinear dynamics are possible if strong salt concentration gradients are confined in microstructures. Much of the recent work has focused on Dukhin’s second-kind electro-osmosis [6, 7] and the Rubinstein-Zaltzman instability [8, 9] near electrodialysis membranes [10] and nanochannels [11, 12]. Similar effects were also observed in packed beds of particles [13, 14]. In all of these cases, the transport of ions across a selective surface depletes the salt concentration and causes nonlinear electrokinetic phenomena in electric double layers (EDLs) sustaining normal current.

In contrast to these studies, our focus here is on the effect of tangential current in the EDL [15, 16, 17], which has a long history, prior to microfluidics. In 1905, Smoluchowski [18] noted that surface conduction can influence electrokinetic phenomena in thin capillaries, especially a low salt concentration. Formulae for surface conduction based on the Gouy-Chapman model of the double layer were derived by Bikerman [19] and Urban et al. [20], and general surface conservation laws were developed by Overbeek [21], Henry [22], and Deryagin and Dukhin [23]. To measure the importance of surface conduction, Bikerman identified the following dimensionless group [24]

\[ \text{Du} = \frac{\kappa_s}{\kappa_0 h} \]

where \( \kappa_s \) is the conductivity of the neutral bulk solution, \( \kappa'_0 \) is the additional “surface conductivity” due to excess ions in the EDLs [19, 20, 16], and \( h \) is a geometrical length scale, such as the channel width or particle size. In honor of Dukhin’s contributions to the theory of surface conduction in electrophoresis, the dimensionless group \( \text{Du} \) has come to be known as the “Dukhin number” [15].

The competition of surface and bulk conduction in a microchannel is now well understood at the level of linear response [25, 26, 15], but recently a surprising nonlinear response was discovered. Mani, Zangle and Santiago showed that, under certain conditions, surface conduction can produce a localized salt concentration gradient propagating through a microchannel, away from a nanochannel junction [27, 28]. By deriving a one-dimensional equation for thin EDLs (the “Simple Model”) and applying the method of characteristics, they explained this phenomenon mathematically as shock propagation in the concentration profile, analogous to pressure shocks in gases [27]. The theory was able to predict, for the first time, the propagation of enrichment and depletion shocks in etched glass microchannels on either side of a nanochannel [28]. It is possible that this phenomenon plays a role in earlier observations of sharp concentration gradients in more complicated microchannel/nanochannel geometries [29], but these experiments involve deeper channels, transverse electro-osmotic and pressure-driven flows [30, 31], and in some cases, nonlinear electro-osmotic vortices, reminiscent of the Rubinstein-Zaltzman instability [11], which may obscure any effects of surface conduction.

In this paper, we focus on the new surface-conduction dominated regime and develop a general theory of “desalination shocks” in complex microstructures, such as non-uniform microchannels or porous media. We shall see that altering the confining geometry can strongly influence (and sometimes eliminate) desalination shocks, and yet, simple macroscopic dynamics can be recovered by volume-averaging in slowly varying microstructures. We begin by describing the basic
Basic physics of desalination shocks

Dynamical regimes. We start with the Simple Model for propagation of salt gradients in a system of parallel channels which was recently developed by Mani et al. [27]. Fig. 1A shows schematics of an electrokinetic system consisting of a nanochannel in series with two microchannels. Mani et al. [27] and Zangle et al. [28, 32] conducted experimental and theoretical analysis of this system and showed that the nanochannel can give rise to propagation of concentration shocks through its neighboring microchannels. The figure shows propagation of a depletion zone from the nanochannel through the left-side microchannel; there is also an enrichment zone propagation on the right-side, but in this paper we only focus on the depletion zone, which involves strong nonlinearity.

There are two distinct physical phenomena associated with this system. The first phenomenon, is initiation of a depletion zone; and the second phenomenon is propagation of this zone into the microchannel in the form of concentration shock. While the first phenomenon always occurs, the second one occurs under certain conditions in terms of wall charge and ion mobility [27]. The initiation phase arises due to the imbalance of current carriers in the nanochannel [33]. Dominance of the wall-shielding counter-ions versus co-ions in the nanochannel allows for selective passage of counter-ions and gives rise to the well known concentration polarization effect. We here briefly note that it is not necessary to have a nanochannel to trigger this phenomenon; other selective elements such as electrodes or membranes can also trigger the first phase as schematically shown in Fig. 1B. If the nanochannel causes enough depletion, and if the surface charge is of the correct sign, the propagation phenomenon will then occur [27]. The propagation phase is in the form of a “desalination” shock, which is entirely sustained by the microchannel.

A natural starting point to describe this system is the Simple Model of Mani et al [27] for a binary electrolyte in a flat microchannel with thin double layers at constant current. Later we show that this model emerges as a special case of a general volume-averaged formulation for porous microstructures. Without loss of generality, let us assume a negative surface charge density, \( \sigma_s < 0 \), on the walls of the microchannel. We begin by recasting the model in terms of the “neutral portion” of the bulk conductivity (in a section-averaged sense),

\[
\kappa_b = \varepsilon^2 (z_+ \nu_+ + z_- \nu_-) z_- c_-,
\]

proportional to the co-ion concentration, and an effective surface conductivity,

\[
\kappa_s = -2z_- \nu_- e \sigma_s,
\]

associated with the remaining counter-ions required to shield the wall charge. As we shall see the same parameters emerge for the case of general microstructure, with the exception that the factor of 2 here is used for convenience to account for top and bottom walls in a flat microchannel. In these definitions, \( c_- \) is the co-ion concentration, \( z_\pm e \) are the charges of the ions, and \( \nu_\pm \) are the ion mobilities.

It is important to stress that what we call \( \kappa_s \), which is related to the difference between co- and counter-ion concentrations (screening the surface charge), is not the same as \( \kappa_b \), the surface conductivity. The latter is defined as the excess conductivity due to sum of co- and counter-ion concentrations in the EDLs relative to the quasi-neutral bulk solution [16, 34]. Only in the limit of strong depletion of the bulk (\( \kappa_b h \ll \kappa_s \)), in which most of the ions in the EDLs are the wall-shielding counter-ions, does the effective surface conductivity, \( \kappa_s \), become equal to the true surface conductivity, \( \kappa_b \).

The Simple Model of Mani et al. [27] for a straight microchannel leads to the following nonlinear advection-diffusion equation for the evolution of the bulk conductivity, \( \kappa_b \):

\[
\frac{\partial}{\partial t}(\kappa_b h_b) + \frac{\partial}{\partial x} \left( u \kappa_b + \frac{z_- \nu_- e I \kappa_b}{h_b \kappa_b + \kappa_s} \right) = \frac{\partial}{\partial x} \left[ h_D \frac{\partial \kappa_b}{\partial x} \right],
\]

where \( D \) is the effective diffusivity, \( u \) is the mean bulk velocity (electro-osmotic plus pressure driven), \( I \) is current per unit width, and \( h \) is the channel height. If the EDL effects (the term with \( \kappa_b \)) can be neglected, Eq. 2 reduces to the classical linear advection diffusion for bulk conductivity [1]. The nonlinear flux,

\[
z_- \nu_- e I \kappa_b / (\kappa_b + \kappa_s),
\]

can be physically interpreted as the advection of \( \kappa_s \) due to electromigration. To see this more clearly, we note that \( I / (\kappa_b + \kappa_s) \) is the ratio of the current to total conductivity of the channel and hence equal to the axial electric field. The field multiplied by \( z_- \nu_- e \) yields an electromigration velocity that advects the surface conductivity, \( \kappa_s \). Gradient of this flux term is responsible for exchanges between EDL and the bulk, which are schematically depicted in Fig. 1C.

Dimensionless formulation. The following dimensionless variables can be used to describe the system:

\[
\tilde{\kappa} = \frac{\kappa_b}{\kappa_{b\infty}}, \quad \tilde{x} = \frac{xu}{D}, \quad \tilde{t} = \frac{tu^2}{D},
\]

where \( \kappa_{b\infty} \) is the bulk conductivity in the reservoirs connecting to the channel system. This choice makes sense whenever there is a significant net flow in the system. In the case of a “dead end” channel with \( u = 0 \), e.g. capped by a membrane or electrode, we would instead choose a length \( L \) to scale position and scale time to \( L^2 / D \), as reported by Dydek et al. [35]. In this paper, without loss of generality, we shall proceed to use the advective scalings (Eq. 3), since our focus is on the nonlinear dynamics.

With these definitions, for a constant-height microchannel Eq. 2 takes the dimensionless form

\[
\frac{\partial \tilde{\kappa}}{\partial \tilde{t}} + \frac{\partial}{\partial \tilde{x}} \left( \tilde{\kappa} + \tilde{I} \tilde{\rho}_s \right) = \frac{\partial^2 \tilde{\kappa}}{\partial \tilde{x}^2},
\]

where two fundamental dimensionless groups appear. The first parameter,

\[
\tilde{I} = \frac{z_- \nu_- e I}{u \kappa_{b\infty}},
\]

is the ratio of electrodiffusion velocity, \( z_- \nu_- e I / h \kappa_{b\infty} \), to the characteristic velocity, \( u \). In systems where electro-osmotic flow dominates, such as the one shown in Fig. 1A, the parameter \( \tilde{I} \) is typically \( O(1) \) and does not play an important role.
role in controlling the dynamics. The second, more important, parameter in Eq. 4 is a dimensionless surface charge,
\[ \hat{\rho}_s = \frac{\kappa_s}{\hbar \kappa_{boc}} = \frac{2b(\sigma_s)}{1 + \frac{\sigma_s}{\kappa_{boc}} - \text{const.}} \]  

[6]

Below, the same parameter \( \hat{\rho}_s \) is defined more generally as the ratio of volume-averaged surface charge to bulk counter charge in a porous microstructure. With our notation the dimensionless parameter \( \hat{\rho}_s \) in Eq. 6 resembles the Dukhin number, \( D_* \), in Eq. 1, but, as discussed above, they are not the same, except in the limit of strong depletion \( \hat{\rho}_s \), \( D_* \gg 1 \).

For typical concentrations in aqueous solutions, \( \hat{\rho}_s \) is very small for microchannels \( (h \sim 1 \mu m) \), suggesting that the nonlinear term in Eq. 4 can be neglected. One mechanism that can activate the nonlinear term (and produce shocks) in microchannels is to locally decrease \( \tilde{k} \) to very small values of order \( \hat{\rho}_s \). This is the crucial role that the selective surface (nanochannel, membrane, or electrode) plays in these systems.

As the shock propagates, it leaves behind a region with orders of magnitude lower salt concentration. In other words, propagation of the shock acts to desalinate the bulk electrolyte. For a microchannel with constant cross section, the shock maintains its constant speed as long as the applied current and the flow rate are maintained constant [27]. In the next two sections, we analyze the dynamics of desalination shocks in systems with non-uniform geometries.

### Weakly varying microstructures

#### Variable channel width

We first consider propagation of desalination shocks in wide channels with constant height, but weakly varying width, as shown in Fig. 2. We can modify Eq. 2 to account for variation of width by simply scaling all the appropriate flux terms with \( w \):

\[ \frac{\partial}{\partial t}(w\kappa_s) + \frac{\partial}{\partial x} \left( w\kappa_b + w\kappa_s \right) = \frac{\partial}{\partial x} \left[ w\rho \frac{\partial \kappa_s}{\partial x} \right]. \]  

[7]

To be able to neglect the transverse fluxes and reduce the system to one-dimensional PDE we assumed \( dw/dx \ll 1 \), which is a standard assumption of lubrication theory. The gradually varying width assumption imposes an additional condition, which physically means that the width does not change much over the axial thickness of the shock. We use \( w_0 \) and \( I_0 \), evaluated at \( x_0 \) (shock location at \( t_0 = 0 \)) to nondimensionalize Eq. 7. \( w \) can be nondimensionalized using \( w_0 \). Noting that \( w\kappa \) and \( Iw \) are constant in \( x \) due to conservation of mass and current, Eq. 7 can be nondimensionalized to

\[ \frac{\partial}{\partial t}(\tilde{w}\kappa) + \frac{\partial}{\partial \tilde{x}} \left( \tilde{w} + \tilde{I}_0 \right) = \frac{\partial}{\partial \tilde{x}} \left[ \tilde{w} \frac{\partial \tilde{\kappa}}{\partial \tilde{x}} \right]. \]  

[8]

Equation 8 has the trivial boundary condition of \( \tilde{\kappa}_{-\infty} = 1 \). We also use a Dirichlet boundary condition of \( \tilde{k}(\tilde{x} = 0) = \tilde{k}_d = O(\hat{\rho}_s) \), which represents a depletion boundary, initiated by a selective element next to the channel. We seek a solution of the form

\[ \tilde{k}(\tilde{x}, \tilde{t}) = \tilde{f}(\eta) = \tilde{f} \left( \frac{\tilde{x} - \tilde{x}_s(\tilde{t})}{\tilde{l}_s(\tilde{t})} \right), \]  

[9]

where \( \tilde{x}_s \) represents the shock location and \( \tilde{l}_s \) is the shock length or axial thickness. The profile of \( \tilde{f} \) satisfies an ODE, yet to be obtained. Since this profile should look like a shock we have, \( \tilde{f}(\eta \ll -1) \approx 1 \) and \( \tilde{f}(\eta \gg 1) \approx \kappa_d \). We propose a solution for \( \tilde{x}_s(\tilde{t}) \) and \( \tilde{l}_s(\tilde{t}) \) by speculating that the local shock length is proportional to the local channel width and its speed is inversely proportional to the width:

\[ \frac{d\tilde{x}_s}{d\tilde{t}} = \frac{\tilde{V}}{\tilde{w}(\tilde{x}_s(\tilde{t})), \tilde{l}_s(\tilde{t}) = \tilde{w}(\tilde{x}_s(\tilde{t}))}, \]  

[10]

where \( \tilde{V} \) is the dimensionless shock speed at \( t = t_0 \). By substituting Eq. 10 into Eq. 9, then into the governing equation (Eq. 8), and ignoring variations of \( \tilde{w} \) over the shock thickness we obtain the following ODE for \( f \):

\[ \left( 1 - \tilde{V} \right) \tilde{f} + \frac{\tilde{I}_0 \tilde{\rho}_s}{\tilde{f} + \tilde{\rho}_s} = \tilde{f}' \]  

[11]

To compute the constant \( \tilde{V} \), we can integrate Eq. 11 from \( -\infty \) to \( +\infty \) and use the boundary conditions. Since \( f' = 0 \) in the limits, we obtain

\[ \tilde{V} = 1 - \frac{\tilde{I}_0 \tilde{\rho}_s}{\tilde{k}_d + \tilde{\rho}_s} + O(\hat{\rho}_s). \]  

[12]

Note that shock propagation would be possible only for negative \( \tilde{V} \). This can be accommodated only if sufficient depletion is introduced at the boundary \( (\tilde{k}_d = O(\hat{\rho}_s)) \).

In a dimensionless sense this solution implies that the shock velocity scales with \( u_0 w_0 / w = u \), which is the local flow velocity (but here in opposite direction of propagation); and the shock axial thickness scales as \( Dw/(u_0 w_0) = D/u \) which is the local advection-diffusion length scale proportional to local cross sectional area. Integrating Eq. 10 yields

\[ \int \tilde{w}(\tilde{x}_s) d\tilde{x}_s = \tilde{V} \tilde{l}, \]  

[13]

which indicates that the rate of sweeping the volume of the channel by the shock is constant. This also makes sense from the global conservation law point of view: Very far from the shock, at the channel boundaries, the flux term, \( \tilde{k}(\tilde{l}_s(\tilde{t})) / (\tilde{k}_d + \tilde{\rho}_s) \), does not change with time and the diffusion flux is negligible. From global conservation, the depletion of ions inside should balance the difference of the fluxes at the boundaries. Therefore, the depletion rate should be constant, implying the rate of sweeping the volume by the shock should be constant.

#### Variable channel perimeter and cross-sectional area

This powerful observation can be generalized to more complicated microstructures such as the ones shown in Fig. 3. In this case we deal with a microstructure with gradually varying cross section parameterized by its cross-sectional area, \( a(x) \), and perimeter \( p(x) \). These respectively represent how surface and perimeter fluxes would scale. The governing equation for this case is

\[ \frac{\partial}{\partial t}(a \kappa_s) + \frac{\partial}{\partial x} \left( Q \kappa_s + \frac{(pr_s)(z\nu \cdot e)(\mathcal{I})}{ak + pr_s} \right) = \frac{\partial}{\partial x} \left[ aD \frac{\partial \kappa_s}{\partial x} \right], \]  

[14]

where \( Q \) is the volume flow rate and \( \mathcal{I} \) is the net current through the system. Again, as a shock propagates in this channel, it sweeps the volume of the channel at a constant rate independent of complexities of \( a(x) \) and \( p(x) \). We note that the earlier case of constant-height channels, with variable-width (with \( w \gg h \)), would be a special case in which both area and perimeter scale with \( w \). For that case we showed that the shock axial extent would be proportional to local area of the channel.
For general $a$ and $p$ however, the evolution of shock length is not as simple. It turns out that even a solution with the form presented by Eq. 9 is not valid any more. In this general case, different regions of the shock can scale differently. We here only report the analytical solution to the shock profile and refer the reader to the supporting information for details of the derivation. One can show that $\tilde{\kappa}$ changes as a function of axial coordinate according to the following relation
\[
\begin{align*}
\tilde{\kappa} &= \ln(1 - \tilde{\kappa}) - (\tilde{\kappa}_a + \tilde{\rho}_s) \frac{\tilde{p}}{\tilde{a}} \ln \left( \frac{\tilde{\kappa} - \tilde{\kappa}_a \tilde{p}}{\tilde{a}} \right)
\end{align*}
\]
where $\tilde{I}, \tilde{\kappa}_a, \text{and} \tilde{\rho}_s$ are constants here, and $\tilde{a}$ and $\tilde{p}$ are gradually varying local area and perimeter (nondimensionalized by their reference values). With $\tilde{a}$ in the denominator of the left-hand-side, this form indicates that the shock axial thickness scales with local $\tilde{a}$, but its shape depends on parameter $\tilde{p}/\tilde{a}$. The right-hand-side involves two terms: The first term, $\ln(1 - \tilde{\kappa})$, is dominant in high concentration region ($\tilde{\kappa} \gg \tilde{\rho}_s$); the second term, which involves $\tilde{p}/\tilde{a}$ as a parameter, is of order $O(\tilde{\rho}_s)$ and is dominant in low concentration zone of the shock. A plot of the shock profile together with these two asymptotic profiles are presented in Fig. S2 in the supporting information.

From physical standpoint it is worth noting that the asymptotic profile of the shock on the high-concentration side,
\[
\tilde{\kappa} \sim 1 - \exp \left[ \frac{\tilde{I} \tilde{\rho}_s}{\tilde{\kappa}_a + \tilde{\rho}_s} \right]
\]
is governed by axial diffusion and a low-concentration boundary condition, moving against the bulk flow. The nonlinear transport associated with surface conductivity is negligible through this high-conductivity zone, although it plays a role in determining the velocity. The same propagating exponential concentration profile of Eq. 16 also arises in other situations, such as dendritic electrodeposition [36, 37], where counter-ions are removed by convection-diffusion-reaction processes at the dendrite tips [38], rather than by surface conduction.

**Similarity solutions for power-law channel width**

**Intermediate asymptotics.** In this section we consider the constant-height channels again, but with power law growth of their width, $\tilde{w} = (\tilde{x}^\gamma)$, as shown in Fig. 4. Here the width variation is not necessarily gradual and may change over the shock axial extent. We are interested in solutions to Eq. 8 at large enough times to approach a self-similar form. Such “intermediate asymptotic” solutions [39] with power-law monomial scalings are expected based on dimensional analysis [40], due to the lack of any natural length scale in the problem. We seek asymptotic solutions of the form
\[
\tilde{\kappa} = \tilde{f}(\eta) = \tilde{f}(\frac{\tilde{x} + C \tilde{t}^\alpha}{\tilde{t}^\beta}).
\]
which characterize features that advect with the scaling $\tilde{t}^\alpha$ as they enlarge (thicken) with the scaling $\tilde{t}^\beta$. Our objective is to find $\tilde{f}$ and $\tilde{\alpha}$ as functions of $\tilde{\beta}$ and $\tilde{\kappa}$, which are related to the growth rate of the structure; $\alpha < \beta$ indicates a diffusion-like spreading, in which advection is not observable due to the fast growth of the structure itself. Substituting this solution into Eq. 8, and simplifying results in
\[
\begin{align*}
\left[ \frac{1}{\tilde{t}} \left( C \tilde{t}^\alpha - \eta \tilde{t}^\beta \right) \right]^\gamma \left( C \alpha \tilde{t}^\alpha - \beta \eta \tilde{t}^\beta \right) + \gamma \left( C \tilde{t}^\alpha - \eta \tilde{t}^\beta \right)^{\gamma-1} f' &= 0, \\
\left( f + \frac{\tilde{I} \tilde{\rho}_s}{f + \tilde{\rho}_s} \right)' &= \frac{(C \tilde{t}^\alpha - \eta \tilde{t}^\beta)^{\gamma/\beta}}{\tilde{t}^\beta} f''.
\end{align*}
\]

In the large $\tilde{t}$ limit appropriately selected $\alpha$ and $\beta$ would reduce this equation to an ODE for $f$. Table 1 summarizes the resulting $\alpha$ and $\beta$ for different $\gamma$ scenarios. Following Bazant and Stone [41], one can systematically check that these are the only scalings that satisfy the boundary conditions, but we omit such mathematical details here. Note that for the case $\gamma < -1$, the total volume of the channel is finite, and an intermediate asymptotic limit does not exist.

**Exponential shock propagation.** In the singular case of $\gamma = -1$ the formal values of $\alpha$ and $\beta$ are infinite. Under this condition the correct solution would be shock propagation with exponential acceleration in time and the correct similarity variable is $\eta = (\tilde{x} + e^{\lambda \tilde{t}})/e^{-\alpha \tilde{t}}$. In the limit of large $\tilde{t}$ the PDE can be transformed to the following ODE:
\[
\left[ 1 + \alpha' f + \frac{\tilde{I} \tilde{\rho}_s}{f + \tilde{\rho}_s} \right]' = f''.
\]

Similar to what observed in Eq. 11, the value of $\alpha'$ can be obtained by integrating the above equation from $-\infty$ to $+\infty$ and using the boundary conditions.
\[
\alpha' = \frac{\tilde{I}}{1 + \tilde{\kappa}_a \tilde{\rho}_s} - 1 + O(\tilde{\rho}_s).
\]

The parameter $\alpha'$ can be interpreted as the inverse of the time scale for exponential propagation and spreading of the concentration profile.

**Power-law shock propagation.** For $-1 < \gamma < 1$ the problem has a power law similarity solution with $\alpha = 1/(\gamma + 1)$ and $\beta = \gamma/(\gamma + 1)$. Note that for this range $\alpha > \beta$ and thus the solution indicates shock propagation. In the limit of large $\tilde{t}$ Eq. 18 reduces to the following ODE:
\[
\left[ \left( 1 + \frac{\gamma^{\gamma+1}}{\gamma + 1} \right) f + \frac{\tilde{I} \tilde{\rho}_s}{f + \tilde{\rho}_s} \right]' = C \tilde{t}^{\alpha'} f''.
\]

Interestingly, in the limit of $\gamma = 1$ this solution leads to $\alpha = \beta = 1/2$, which represents the onset of transition towards a diffusive propagation.

**Diffusive shock propagation in a wedge (critical case).** The case of $\gamma = 1$ represents a wedge-like channel whose width grows with constant slope as shown in Fig. 4C. After the case of a straight channel ($\gamma = 0$), this case may be the most relevant for lab-on-a-chip systems. Note that for $\gamma = 1$ equations can be represented in cylindrical coordinates (with $\tilde{x}$ interpreted as radius); the lubrication theory assumption $\left( d\tilde{w}/d\tilde{x} \right) \ll 1$ is not necessary to enable reduction of the system to one-dimensional PDE. Therefore, the wedge angle can be any number from 0 to $2\pi$.

For $\gamma = 1$ the similarity variable reduces to $\eta = \tilde{x}/\sqrt{\tilde{t}}$, which shows diffusive scaling in time. Equation 18 reduces to
\[
- \frac{\left( \frac{\eta}{2} + \frac{\gamma}{\eta} \right) f'' - \frac{1}{\eta} \left( \frac{\tilde{I} \tilde{\rho}_s}{f + \tilde{\rho}_s} \right)'}{f'} = f''.
\]

but there is still some effect of surface conduction, measured by $\tilde{\rho}_s$.

**Linear diffusion (no shocks).** For all values of $\gamma > 1$ the similarity variable will also be $\eta = \tilde{x}/\sqrt{\tilde{t}}$ and Eq. 18 reduces to the following ODE, which corresponds to linear diffusion:
\[
- \frac{\left( \frac{\eta}{2} + \frac{\gamma}{\eta} \right) f''}{f'} = f''.
\]
Note that there is no longer any effect of surface conduction \((\dot{\rho}_s)\) on the intermediate asymptotic similarity solution.

This ODE (Eq. 23) is valid for large \(t\), when the advective flux term in Eq. 18 becomes negligible compared to other terms. However, for very large \(t\) the diffusive front may reach locations of the channel with large \(dw/dx\) and the lubrication theory assumption may not be valid any more. As a result Eq. 23 will be valid for a range in time described by:

\[
1 < \left( \frac{ta_0^2 D}{\gamma} \right)^{\frac{1}{2}} < \frac{D}{\gamma a_0 t_0}. \tag{24}
\]

For durations much larger than the upper bound, the channel span would have a fast growth, \(dw/dx \gg 1\). In this range, the channel may be approximated by a 180-degree wedge and propagation can be modeled by the axisymmetric case \((\gamma = 1)\).

Numerical examples of similarity solutions for a widening \((\gamma = 0.75)\) and a contracting \((\gamma = -0.25)\) in comparison to the solutions to the full Eq. 8 are presented in Fig. S1 in the supporting information. It is verified that after a short transient time the full-solutions collapse into 1D plots described by the similarity solutions.

Desalination shocks in porous media

Volume-averaged transport equations. In this section, we derive general, macroscopic transport equations for concentration polarization and desalination shocks in microchannels and porous media. The resulting model has a similar form as the Simple Model of Mani et al. \[27\] for straight microchannels (see Fig. 5), only the derivation is much more general and provides various nonlinear corrections. We simply require that the geometrical and electrochemical properties of the microstructure vary sufficiently slowly to justify a (formal) volume averaged theory.

Let \(c_i\) be the mean volume-averaged concentration of ion species \(i\) in the pores (number / pore volume), and \(D_i\) the effective diffusivity within the porous matrix \[1, 42\]. Let \(u\) be the mean (mass averaged) fluid velocity. Conservation of species at the macroscopic continuum level is then expressed by the Nernst-Planck equations:

\[
\frac{\partial c_i}{\partial t} + u \cdot \nabla c_i = \nabla \cdot \left( D_i \left( \nabla c_i + \frac{q_i}{kT} \nabla \phi \right) \right), \tag{25}
\]

where we use the Einstein relation to express the mobility of species \(i\) as \(v_i = D_i/kT\). However, a more general model, which we describe in the supporting information, would involve non-constant diffusivities, independent of mobilities, which can arise due to variation in the porous structure and/or to account nonlinear flow effects such as Taylor dispersion. Here, we focus on constant-property media and propose a simple model that captures the essential physics.

Consider a porous solid material of porosity \(\epsilon_p\) (pore volume / total volume) and area density \(a_p\) (pore area / total volume) filled with an electrolyte. The walls of the pores have a fixed charge density \(\sigma_s\) (charge / pore area). At the macroscopic continuum scale, the surface charge appears as a fixed background charge density (charge / pore volume) \(\rho_s\) given by

\[
\rho_s = \frac{\sigma_s}{h_p} = \frac{\sigma_s a_p}{\epsilon_p} \tag{26}
\]

where \(h_p = \epsilon_p/a_p\) is an effective pore size, equal to half the pore radius for a cylindrical pore. We simply enforce electroneutrality at the macroscopic continuum scale,

\[
\epsilon_p \rho + a_p \sigma_s = 0 \quad \Rightarrow \quad \rho = \sum q_i c_i = -\rho_s \tag{27}
\]

where \(\rho\) is the mean ionic charge density, which is equal and opposite to the surface charge density, \(\rho_s\). The macroscopic, volume-averaged electroneutrality condition (Eq. 27) implicitly determines the mean electrostatic potential in Eq. 25.

Let \(c = \sum q_i c_i\), the total ionic charge (regardless of sign). For \(|\rho| = |\rho_s| < c\), we recover the standard model for a quasi-neutral bulk electrolyte, which leads to the (ambipolar) diffusion equation for the neutral salt concentration \[1\]. In the opposite limit, \(|\rho_s| \approx c\), we recover the standard model for a bulk ion-exchange membrane or solid electrolytes \[43, 44, 45\]. In contrast, our focus is on the intermediate regime, where \(|\rho_s| < c\), which generally introduces nonlinearity due to electromigration of the diffuse ionic charge, which screens the fixed background charge.

Binary electrolyte. The simple hypothesis presented by Eq. 27 could be applied to any situation involving porous media described by effective, macroscopic Nernst-Planck equations (Eq. 25). For concreteness, we proceed to develop the model for the canonical case of a dilute, asymmetric binary electrolyte \((i = +, -)\) with arbitrary ionic charges, \(q_{\pm} = \pm z_{\pm} e\). With these simplifications, our equations take the form,

\[
\frac{\partial c_+}{\partial t} + u \cdot \nabla c_+ = D_\pm \left[ \nabla^2 c_\pm \pm z_{\pm} e \nabla \cdot \left( \nabla \phi \right) \right] \tag{28}
\]

\[
0 = z_+ e c_+ - z_\pm e c_\pm + \rho_s \tag{29}
\]

where \(\phi = e\phi/kT\) is the dimensionless potential, scaled to the thermal voltage. Without loss of generality, let us assume that the surface charge is negative, \(\rho_s < 0\), and use Eq. 29 to replace the ion concentrations \(c_+\) and \(c_-\) with the neutral portion of the salt concentration in the bulk (excluding wall shielding charge)

\[
c_b = z_+ c_+ + z_- c_- = 2 z_- c_- \tag{30}
\]

In the limit of zero surface charge, this reduces to the total concentration of charges \((c_b \rightarrow z_+ c_+ + z_- c_-)\) in a neutral electrolyte. In the opposite limit of a fully depleted bulk electrolyte with nonzero surface charge, this quantity vanishes, since only counter-ions remain within the EDLs of the microstructure \((z_+ c_+ \rightarrow -\rho_s)\). Therefore, the variable \(c_b\) measures the amount of “free conductivity” that can be removed from the microstructure (i.e. contributing to desalination), without disturbing the screening of the fixed surface charge by counter-ions. In terms of these variables, the PDEs can be written in the following form

\[
\frac{\partial c_b}{\partial t} + u \cdot \nabla c_b = \nabla \left[ \nabla^2 c_b - \frac{z}{\epsilon} \nabla \cdot \left( \rho_s \nabla \phi \right) \right] \tag{31}
\]

\[
0 = \nabla \cdot j \tag{32}
\]

where \(j\) is the volume averaged current density (given below); \(\nabla\) is the ambipolar diffusivity of a binary electrolyte \[1\] (see the supporting information for the general form of \(\nabla\) and \(\epsilon\)).

It is clear that in this model, any nonlinear response is entirely due to the fixed surface charge, since a linear advection-diffusion equation for \(c_b\) is recovered from Eq. 31 if and only if \(\rho_s = 0\). If any such charge exists in the microstructure, then the second term in Eq. 31 survives, and the dynamics of the ionic transport will be coupled to that of the potential \(\phi\), which generally satisfies a PDE (Eq. 32) enforcing the conservation of charge. The nonlinearity becomes apparent from the volume-averaged current density in Eq. 32, which takes the form

\[
\frac{e}{kT} (j + \rho_s u) = -\beta \nabla \nabla \phi_n - \left[ \kappa_b + \frac{\rho_s}{h_p} \right] \nabla \phi \tag{33}
\]
where the second term on the left is the convection of charge; the first term on the right is the diffusion current, controlled by the parameter

$$\beta = \frac{D_s - D_c}{kT(z_+\nu_+ + z_-\nu_-)}$$  \[34\]

which measures the asymmetry of the electrolyte; the second term on the right hand side of Eq. 33 is Ohm’s law, where the total conductivity is broken into two parts: neutral portion of the bulk, and surface (excess counter-ion) contributions. These are respectively:

$$\kappa_b(c) = \frac{(z_+\nu_+ + z_-\nu_-)e^2c}{2}$$  \[35\]

$$\kappa_s = z_+\nu_+ c|\sigma_s|$$  \[36\]

The connections to the special case discussed by the Simple model of Mani et al. [27] becomes now more apparent as these definitions lead to the same dimensionless surface charge \(\tilde{\rho}_s\) given at the beginning of the paper for a flat microchannel (noting that \(h_p = h/2\) for flat channels).

**Uniform current.** To illustrate the use of these equations, we consider passing a uniform current density \(j = j(t)x\) through the porous medium. We solve Eq. 33 for the electric field and substitute back into Eq. 31 to obtain a single, nonlinear PDE for bulk conductivity \(\kappa_b(x, t)\):

$$\frac{\partial \kappa_b}{\partial t} + \nabla \cdot \left[ u \kappa_b(x) \right] = \frac{\partial}{\partial x} \left[ D_s(\kappa_b) \frac{\partial \kappa_b}{\partial x} \right]$$  \[37\]

This general one-dimensional PDE for uniform current in a microstructure is similar to that obtained by Mani et al. in their Simple Model for a flat microchannel with thin double layers (Eq. 2), with the same form for the nonlinear term on the left hand side. One qualitative difference is that we include the convective contribution of the EDL charge to current \((\rho, u)\). Another qualitative difference is that the macroscopic axial diffusion coefficient \(D_s\) is not constant, but depends on conductivity:

$$D_s(\kappa_b) = \mathcal{D} \left( 1 - \frac{z_+(D_s - D_c)}{2z_+D_s} \frac{\kappa_b}{\kappa_b + \kappa_s} \right)$$  \[38\]

In the propagating shock regime, this nonlinear term will only affect shock structure, but not the shock dynamics. It may have a significant effect, however, on the diffusion regime prior to strong depletion, as well as the eventual steady state, in an asymmetric electrolyte.

**Fluid flow.** There are many possible nonlinear effects of fluid flow, especially in higher dimensions. Assuming thin channels in a slowly varying microstructure, the simplest approximation is to enforce macroscopic incompressibility,

$$\nabla \cdot u = 0$$  \[39\]

and postulate linear response to gradients of pressure, potential and concentration at the macroscopic continuum scale,

$$u = -K_R \nabla p - K_E \nabla \theta - K_c \nabla \ln c$$  \[40\]

The first term is Darcy’s law, the second electro-osmotic flow, and the third diffusio-osmotic flow, each of which in principle have tensorial coefficients in an anisotropic medium [46]. Through these equations, the electro-osmotic flow and concentration polarization in response to an applied voltage produces a pressure-driven flow, which in turn affects the concentration, via our theory above. In one dimension, the mean flow remains constant, but other complexities can arise (such as Taylor dispersion [47] discussed in the supporting information).

**Conclusion and Outlook**

In summary, we have developed a general theory of ion transport in microchannels and porous media, focusing on the new nonlinear regime where surface conduction dominates convection in competing with bulk diffusion. For slowly varying microstructures, the equations support propagating shocks, as well as similarity solutions with power-law scalings. Even in the presence of microscopic inhomogeneities, we expect that these solutions are stable attractors of the nonlinear dynamics [48], similar to reaction-diffusion fronts in porous media [49]. The multidimensional problem is more complicated, especially in situations where the current is misaligned with the fluid velocity. Even when the macroscopic dynamics is stable, the microscopic dynamics within the microchannels may involve electro-osmotic instabilities and convective mixing with increasing channel thickness [35]. We believe this system provides many promising directions for research in applied mathematics.

Beyond the implications for basic science and mathematics, there may be important engineering applications for this work. As suggested by our choice of nomenclature, a natural application would be to water purification and desalination. Our group is currently investigating this concept, theoretically and experimentally, and the results will be reported elsewhere [35].

Our theoretical results could also be applied to DC electro-osmotic pumps, which employ electro-osmotic flow in porous glass frits [50, 51, 52]. Strickland et al. have recently found that concentration polarization can be a key factor in the pump performance [53], but current theories do not account for the formation of concentration gradients or surface conduction. Our volume-averaged equations for concentration polarization in porous media could be directly applied to this situation. As discussed above, we predict analogous nonlinear phenomena in porous media, as in individual microchannels.

Our results may also find applications in micro/nanofluidic systems. We have shown that varying the cross-sectional area, perimeter and/or surface charge of a microchannel provides robust means to control the nonlinear dynamics of transport. In parameter regimes where surface conduction is important (non-negligible \(\tilde{\rho}_s\)), this capability may be useful in microfluidic devices for biological sample preconcentration [30] and seawater desalination [31] consisting of microchannel/nanochannel junctions. During normal operation, complex electrokinetic instabilities have been observed [11] and, together with fast pressure-driven flows [31], electrohydrodynamic phenomena may dominate any effects of surface conduction. Geometrical optimization of microchannel interfaces may also lead to more robust designs for nanofluidic systems [54], e.g. for DNA or protein sequencing or molecular sorting, in this case to inhibit the formation of shocks, which interfere with external control of dynamics within the nanochannel.

Another interesting direction would be to relax the assumption of fixed surface charge, and allow for capacitive charging [55]. Faradaic reactions [56, 45], or induced-charge electro-osmotic flows [57] in microfluidic devices or porous electrodes. Leinweber et al. [58] have observed that metal micropost arrays in thin (1 micron) channels can produce strong concentration polarization and continuous desalination. The effect is driven by surface conduction on ideally polarizable metal cylinders [59]. It is likely that desalination shock phenomena, due to surface conduction on the microchannel walls,
also play a role in shaping the salt concentration profile in these devices.

In the case of porous electrodes, our volume-averaged equations for porous media can be applied to capture effects of surface conduction, but they must be augmented by a charge-voltage relation for the double layer, e.g. using the Gouy-Chapman-Stern model of capacitive charging [34, 55] or the Frankin-Butler-Volmer-Stern model of Faradaic reactions [45]. Porous electrodes are widely used in electrochemical energy storage devices (batteries, supercapacitors, fuel cells, etc.) [56, 1], but we are not aware of any prior work considering surface conduction. Designing the porous microstructure to exploit the nonlinear effects of surface conduction could provide a new means to enhance the power density of portable power sources.

References:
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Table 1. Scaling of desalination shock advancement and thickening with time for a microchannel with power law growth of width. \( \gamma \) is power of growth of channel width with axial coordinate, \( w = (-x)^\gamma \); the shock location is assumed to advance as \( x_s \sim t^\alpha \); and the shock axial thickness grows/shrinks as \( l_s \sim t^\beta \).

<table>
<thead>
<tr>
<th>( \gamma )</th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-1)</td>
<td>exponential</td>
<td>( \frac{1}{2} )</td>
<td>shock/diffuse</td>
</tr>
<tr>
<td>(1, \infty)</td>
<td>exponential</td>
<td>( \frac{1}{2} )</td>
<td>diffuse</td>
</tr>
</tbody>
</table>

![Fig. 1. Schematics of propagation of desalination shocks in microchannels. A shows a series microchannel-nanochannel-microchannel system subject to a constant current, \( I \), and electroosmotic flow rate, \( Q \), as investigated by Mani, Zangle and Santiago [27, 28]. Regions of low concentration are indicated by lighter shading. Figure shows propagation of the depletion shock through the left-side microchannel. Same shocks can be generated by employing a membrane or a nanoporous element instead of the nanochannel as depicted in B. An isolated shock in a microchannel is shown in C with schematics of ionic exchange with the EDLs near the shock.](image)

![Fig. 2. Propagation of desalination shock in a rectangular microchannel with constant cross section (A), and the history of concentration from profiles sampled uniformly in time with \( \Delta t = D/u_0 \) (B). In this case the shock preserves its shape and propagates at a constant rate. In a width-varying channel (C), shock thickness and speed changes as it propagates through different sections of the channel (D). For both cases the channel width is much larger than its height and the figure is not to scale.](image)
Fig. 3. A microstructure with gradually varying cross section.

Fig. 4. (a) Schematics of desalination shock propagation in a contracting microchannel ($\gamma = -1$) is shown in A. Profiles of the shock at different stages indicate that as the shock reaches the narrower regions of the microchannel it gains speed and adopts a sharper axial profile (B). Schematics of propagation in a linearly expanding channel is shown in C. Time-series of the axial profiles indicate that the shock slows down and becomes diffuse towards the end of the channel (D).

Fig. 5. Schematics of desalination shock propagating through a uniform porous microstructure (A). The dynamics of this shock is similar to that propagating in a straight microchannel with the same nondimensional parameter $\tilde{\rho}_s$ (see Eqs 2 and 37. As described in Appendix B, propagation of desalination shocks in nonuniform structures (C) is similar to that in channels with variable cross section (D).