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Pressure-sensitive ion conduction in a conical channel: Optimal pressure and geometry

A fluidic channel allows for the simultaneous transport of solvent, charge, and dissolved salt when connected to two liquid electrolyte reservoirs at different pressures, voltages, salt concentrations, and/or temperatures. Such ionic transport is not only interesting from a fundamental point of view but also for energy harvesting, desalination, and microfluidic applications. In all these devices fluidic channels with dimensions in the nano- and micrometer regime are used, a size range where the influence of surface charge on transport becomes significant due to the relatively large surface-to-volume ratio. This surface charge is key to electrokinetic transduction phenomena, such as the flow of electrolyte by an electric potential difference or the electric (streaming) current induced by flow due to an applied pressure drop. While these electrokinetic transduction phenomena have long been understood, at least in simple channel geometries, in conical pores, exotic transport behaviors, such as electro-osmotic flow inversion, other non-linear flow-effects, and current rectification, have been observed. Such non-linear transport behavior makes conical pores uniquely attractive for biochemical sensing and neuromorphic applications. In this Letter, we analyze the intricate case of a micrometer-sized conical channel exposed to a simultaneous pressure and electric potential drop by means of the well-known Poisson–Nernst–Planck–Stokes (PNPS) equations. We will show that the ionic current in conical nanopores can be either strongly reduced or enhanced by a pressure difference and concomitant flow, resulting in an extremely mechanosensitive ionic diode similar to those present in cell membranes. Such pressure-sensitivity can also be used to optimize power generation in artificial pores. Recent experiments revealed such a non-linear pressure-induced electric transport in conical pores even at micrometer length scales. It was found that the electric current $I(\Delta P, \Delta \psi)$, due to an applied potential difference $\Delta \psi$, is very sensitive to the applied pressure drop $\Delta P$ over the channel. Surprisingly, the observed pressure dependence of the electric conductance occurred at extremely low rather than high pressures. For conical pores it was already observed that, for $\Delta P = 0$, the response of the current $I$ is asymmetric with regard to the sign of $\Delta \psi$ and this so-called current rectification is attributed to concentration polarization. Here, we show that the flow (and hence pressure)-sensitive conductivity for $\Delta P \neq 0$ can also be understood by the concentration-polarization, in contrast to earlier work which suggests that novel mechanisms are needed, such as a bulk space-charge or a non-linear streaming current. Such a flow-sensitive conduction was previously noted in numerical calculations, which, however, ignored electro-osmotic flow that we find to be of great importance.
phase $x \gg L$ and are equal to $\Delta \psi$ and $\Delta P$, respectively, for $x \ll -L$, where $P_0$ is an arbitrary reference pressure. They drive a fluid flow with velocity $\mathbf{u}(x, r)$ and ionic fluxes $j_+(x, r)$, leading to nontrivial concentration profiles $\rho_+(x, r)$. In part (I) of the supplementary material, we present the standard Poisson–Nernst–Planck–Stokes (PNPS) equations and the blocking and no-slip boundary conditions. Together with Gauss’ law for the surface charge, they form a closed set for $\mathbf{u}$, $\psi$, $j_+$, and $\rho_+$. Convenient linear combinations are the total salt concentration $\rho_s = \rho_+ + \rho_-$, the charge density $\rho_e = \rho_+ - \rho_-$, and the associated fluxes $j_k = j_+ + j_-$ and $j_0 = j_+ - j_-$. In equilibrium, i.e., for vanishing $\Delta P$ and $\Delta \psi$, all fluxes vanish and the PNPS equations describe an Electric Double Layer (EDL) with an excess of cations and a depletion of anions close to $r = r_0$ such that the negative surface charge is compensated. The thickness of the EDL is given by the Debye length $\lambda_D = \sqrt{\varepsilon_0 k_b T/2e^2 \rho_b}$.

Inspired by the experimental conditions of Ref. 46, the focus of this Letter will be on the long-channel thin-EDL limit with $L \gg R_0 \gg R_t \gg \lambda_D$ such that EDL-overlap does not play a role. This is in contrast to a large body of literature on non-linear transport in cone-shaped channels, where overlap of the EDL is a key ingredient for current rectification and diodic behavior. We will show that the conical geometry combined with simultaneous pressure- and potential-induced transport leads to an $x$-independent volumetric flow rate $Q = 2\pi \int_0^{R(x)} \mathbf{u}(x, r) r dr$ and electric current $I = 2\pi \int_0^{R(x)} j_0(x, r) r dr$ that satisfies an Onsager-like relation

$$\begin{pmatrix} Q \\ I \end{pmatrix} = \frac{\pi R_0 R_t}{L} \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} \Delta P \\ \Delta \psi \end{pmatrix}. \quad (1)$$

We set out to calculate all elements of the transport matrix $L$ analytically, not only the permeability $L_{11}$ and the electro-osmotic mobility $L_{12} = L_{21}$ but also the electric conductance $L_{22}$ that, as we will see, strongly depends on the applied pressure and voltage drop in agreement with experiments. This pressure-sensitivity is due to highly nontrivial ion concentration profiles that vary on length scales of the channel dimensions as follows from our analytic expression obtained from the PNPS equations. From this, we will find that optimal current rectification requires not only a pressure drop $\Delta P^* = -L_{12} \Delta \psi/L_{11}$ (such that $Q = 0$) but also a universal optimal geometry with $R_0/R_t \approx 0.22$. We solve the PNPS equations for a wide variety of system parameters and show illustrative examples for the standard parameter set inspired by Ref. 46 with tip radius $R_t = 0.17 \mu m$, channel length $L = 10 \mu m$, base radius $R_0 = 1.04 \mu m$, viscosity $\eta = 1 \text{ mPa s}$, dielectric constant 80 times vacuum permittivity, ionic diffusion coefficient $D = 1 \text{ nm}^2/\text{ns}$, and surface charge $\sigma = -0.02 e/\text{nm}^2$, which gives at $\rho_b = 1 \text{ mM}$ a zeta potential of $\zeta = -40 \text{ mV}$ corresponding to a silica surface in contact with an aqueous $1:1$ electrolyte.

In line with the Stokes equation, we find $\mathbf{u}(x, r)$ to contain essentially two contributions. (i) A pressure drop on its own induces a Poiseuille-like flow that is directed toward the (virtual) vertex of the cone for $\Delta P > 0$ or away from it for $\Delta P < 0$. Its contribution $Q_B \equiv (\rho_b R_0/R_t) L_{11} \Delta P/Q$ is independent of $x$ and can be obtained analytically $^{43,46}$ to yield $L_{11} = R_0^2 R_t^2/8\eta(R^2)$, where the angular brackets denote a lateral average $\langle R^2 \rangle = \int_0^\infty R^2 r dr/L = (R_0^2 + R_t^2 + R_0 R_t)/3$. The excellent agreement between the pressure-drop dependence of our linear expression for $Q_B$ and our...
numerically obtained value of $Q$ at $\Delta \psi = 0$ is shown in Fig. S1(a) of part (II) in the supplementary material. (ii) For our negative surface charge, the potential drop $\Delta \psi$ on its own induces an electro-osmotic plug-like flow toward the tip of the cone for $\Delta \psi > 0$ or away from the tip for $\Delta \psi < 0$. We are not aware of an explicit expression in the literature for $L_{12}$ that characterizes the electro-osmotic flow rate $Q_{o} \equiv (\pi R_{b} R_{I}/L)_{12} \Delta \psi$ in a conical pore. Here, we derive an explicit expression for $L_{12}$, which first requires an expression for the cross-section averaged electric field $-\partial_{x} \psi(x)$, see Eq. (S1) of part (II) in the supplementary material, where $\psi(x) = 2 \pi \int_{0}^{R_{b}} \psi(x, r) rdr / \pi R^{2}(x)$. This averaged electric field has to be proportional to the inverse of the cross section $\pi R^{2}(x)$ in order to be divergence free. The proportionality constant follows, in the long-channel limit, from the condition that $\int_{0}^{L} \partial_{x} \psi(x) dx = - \Delta \psi$. This yields

$$\partial_{x} \psi = - \frac{\Delta \psi R_{b} R_{I}}{L} \frac{R^{2}(x)}{R^{2}(x)} \tag{2}$$

which compares well to the numerical results, as illustrated in Fig. S2 of part (II) in the supplementary material. Using the standard electro-osmotic mobility $L_{12} = - \epsilon_{0} \sigma / \eta$ for a cylinder, but now with our laterally varying electric field and radius, we obtain $Q_{o} = \pi R^{2}(x)(-\epsilon_{0} \sigma / \eta) \partial_{x} \psi(x)$ which with Eq. (2) is independent of $x$ and hence represents a valid divergence-free solution for the stationary state. In Fig. S1(b) of part (II) in the supplementary material, we compare this expression for $Q_{o}$ as a function of $\Delta \psi$ with numerical calculations. The agreement is good, although minor deviations on the order of ~10% are visible which we attribute to the approximate nature of our $L_{12}$.

With $L_{11}$ and $L_{12}$ established, we continue with $L_{22}$, for which the total ion concentration $\rho_{i}(x, r)$ is expected to play a major role. In our numerical calculations, we find weak radial variation of $\rho_{i}(x, r)$ outside the EDL-vicinity $r \approx R(x)$, in agreement with Ref. 48. Hence, within the thin-EDL limit, this implies that the cross-sectional averaged concentration $\bar{\rho}_{i}(x)$ is a good proxy for the salt concentration at axial position $x$. If we now define the total salt flux as $J_{x} = 2 \pi \int_{0}^{R_{b}} \bar{\rho}_{i}(x, r) r rdr$, we can insert the diffusive, conductive, and advective contributions of $J_{x}$ as given by the PNPS equations in part (I) of the supplementary material to rewrite the stationarity condition $\partial_{x} J_{x} = 0$ for $x \in [0, L]$ as

$$D \partial_{xx} \pi R^{2}(x) \partial_{x} \bar{\rho}_{i}(x) - 2 \pi R^{2}(x) \sigma \partial_{x} \psi \frac{C_{18}/C_{19}}{k_{o} T} - Q \partial_{x} \bar{\rho}_{i}(x) = 0. \tag{3}$$

Here, we use the radial independence of $\rho_{i}(x, r)$ and $\psi(x, r)$ in the thin-EDL limit as well as the slab-neutrality condition $2 \pi \int_{0}^{R_{b}} \rho_{i}(x, r) rdr = - 2 \pi R^{2}(x) \sigma$ as derived in part (II) of the supplementary material. The slab neutrality condition is an important difference with the analysis presented in Ref. 48, where it was suggested that a bulk space-charge is of key importance for understanding the observed mechano-sensitivity of conical pores. For a given $\Delta \psi$ and $\Delta \psi$, we consider $Q$ and $\partial_{x} \psi(x)$ known from Eqs. (1) and (2), respectively, such that Eq. (3) is an ordinary second-order differential equation for $\bar{\rho}_{i}(x)$; together with its solutions presented below, it constitutes the key result of this Letter. An important role will be played by the conductive contribution $I_{\text{cond}}(x)$ to $J$ given by $I_{\text{cond}}(x) = - 2 \pi D \sigma (\epsilon \Delta \psi / k_{o} T) R_{b} R_{I} / R(x)L$, which varies with $x$ in a conical channel and, thus, acts as a source or sink term in Eq. (3) that sucks ions into the channel for $\Delta \psi < 0$ and pushes them out for $\Delta \psi > 0$.

Given the long-channel limit of interest and the equal salinity of both reservoirs, we solve Eq. (3) with boundary conditions $\bar{\rho}_{i}(0) = \bar{\rho}_{i}(L) = 2 \rho_{b}$, resulting in

$$\bar{\rho}_{i}(x) - 2 \rho_{b}$$

$$= \frac{\Delta \rho}{\Delta \psi} \left[ \frac{x R_{b}}{L R(x)} \frac{\exp \left( \frac{x R_{b}}{L R(x)} \right)}{\exp \left( \frac{R_{b}}{R_{b}} \right) - 1} - 1 \right]$$

$$= \frac{\Delta \rho}{\Delta \psi} \left[ \frac{R_{b}}{2 \rho_{b}} \left( \frac{R_{b}}{R(x)} \left( \frac{x}{L} \frac{R_{b}}{R} \right) + 1 \right) \right]$$

$$= \frac{\Delta \rho}{\Delta \psi} \left[ \frac{R_{b}}{2 \rho_{b}} \left( \frac{R_{b}}{R} \left( \frac{x}{L} \frac{R_{b}}{R} \right) + 1 \right) \right]$$

$$\Delta \rho \equiv \frac{2 \Delta \psi}{R_{I} \sigma e \Delta \psi R_{b}^{2} / k_{o} T}. \tag{5}$$

Thus, $\Delta \rho = 0$ if $R_{b} = R_{I}$ and hence $\bar{\rho}_{i}(x) = 2 \rho_{b}$ in this note. That both Pe and $\rho_{b}$ have a sign and that the dependence on the potential drop is not only accounted for by $\Delta \rho$ but also by $\rho_{b}$ through the electro-osmotic contribution to $Q$ [see Eq. (1)]. Clearly, Eq. (4) reveals concentration variations on length scales on the order of the full channel length $0 \leq x \leq L$ most prominently for smaller $\rho_{b}$. Since the Péclet number quantifies the importance of flow, we can reconcile the discrepancy between works which find electro-osmotic flow to be negligible and others which find it to be important, as the latter concerns a parameter set with small $\Delta \psi \approx 10^{-2} (R_{b} / R_{I})^{2}$ and the latter with large $\Delta \psi \approx 3 (R_{b} / R_{I})^{2}$. For $\Delta \psi = \pm 0.4 V$, which for our standard parameter set gives $\Delta \rho \approx 31$ mMV from Eq. (5), we plot the concentration profile $\bar{\rho}_{i}(x)$ of Eq. (4) in Fig. 2(a) for Péclet numbers between 0 and $\pm 200$. In Fig. 2(b), we plot the salt concentration $(\bar{\rho}_{i})$ laterally averaged over the interval $x \in [0, L]$, which will play a key role in the electric conductivity $\Lambda_{22}$, as a function of the imposed pressure drop $\Delta P$ for the three voltage drops $\Delta \psi = \pm 0.4 V$ (red), 0 V (green), and $-0.4 V$ (blue), as obtained numerically from solutions of the PNPS equations (symbols) and on the basis of a straightforward numerical integration of Eq. (4) (lines). The agreement, although not perfect, is very good especially for $\Delta P > 0$. Our Eq. (4) not only correctly predicts the increase/decrease compared to $2 \rho_{b}$ for a negative/positive potential drop but also the non-monotonic dependence on $\Delta P$; the absolute difference with $2 \rho_{b}$ is largest (and on the order of $30\%$) for $\Delta \psi \approx \pm 10$ mbar, which corresponds in both cases to $\rho_{b} \approx 0$.

The two vertical dashed lines represent the pressure drop $\Delta P = - (L_{11}/L_{12}) \Delta \psi$, where $Q = 0$ and hence $\rho_{b} = 0$ on the basis of Eq. (1), such that the optimal concentration polarization is to be expected. Collecting our earlier results, we find the optimal pressure drop per voltage drop

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about pressure-sensitivity observed in the experiments. In fact, our results square scaling of \( D \) which yields about \( 27 \) mbar/V for the extremely large tip-base ratios \( R_t \gg R_i \) generated by the extrusion of a pipette in the experiments of Ref. 46 (if we assume \( \psi_0 = -40 \) mV common for silica). Clearly, the inverse square scaling of \( \Delta P^* \) with \( R_i \) is key to explaining the dramatic pressure-sensitivity observed in the experiments. In fact, our results suggest even more pressure-sensitivity for larger conical channels, e.g., for \( R_i = 10 \) m, we have \( \Delta P^* \) in the microbar regime, which can already be exerted by the sound of passing traffic\(^{68,69} \). For cases where \( \Delta P \gg \Delta P^* \), concentration polarization is washed out by the flow; variation of current with both pressure and voltage then closely follows Ohmic conduction. As flow suppresses diodic performance, at a static pressure drop, \( \Delta P \neq \Delta P^* \) rectification can also be increased by lowering the dielectric constant \( \varepsilon \) or increasing the viscosity \( \eta \) thereby lowering the electro-osmotic flow rate while keeping \( \Delta \rho \) unchanged.

Now that we have established that Eq. (4) gives a fair account of the salt concentration profile in the channel, we will use it to approximate \( \rho_w^* \). In the thin-EDL limit, the total current \( I \) is dominated by the conductive component \(-(\varepsilon_{\mathbf{k}B}/T)\rho_s(x, r)\partial_x \psi(x, r)\) of \( x \cdot \partial_x (x, r) \) and cross-sectional integration of this current with Eq. (2) and the same thin-EDL limit as before yields \( I_{\text{cond}}(x) = \pi R_t \rho_s \partial_x \psi(x) / (\varepsilon_{\mathbf{k}B} T L) \), which manifestly depends on \( x \) on the basis of Eq. (4). In steady state, this lateral variation of the conductive

\[
\frac{\Delta P^*}{\Delta \psi} = \varepsilon \psi_0 \frac{b (R_i^2 + R_o R_i + R_t^2) R_o}{3 R_t R_i^2} \approx 8 \pi \varepsilon \psi_0 \frac{1}{3 R_t^2},
\]

which yields about \(-32 \) mbar/V for our standard parameter set and about \(-27 \) mbar/V for the extremely large tip-base ratios \( R_t \gg R_i \) generated by the extrusion of a pipette in the experiments of Ref. 46 (if we assume \( \psi_0 = -40 \) mV common for silica). Clearly, the inverse square scaling of \( \Delta P^* \) with \( R_i \) is key to explaining the dramatic pressure-sensitivity observed in the experiments. In fact, our results suggest even more pressure-sensitivity for larger conical channels, e.g., for \( R_i = 10 \) m, we have \( \Delta P^* \) in the microbar regime, which can already be exerted by the sound of passing traffic\(^{68,69} \). For cases where \( \Delta P \gg \Delta P^* \), concentration polarization is washed out by the flow; variation of current with both pressure and voltage then closely follows Ohmic conduction. As flow suppresses diodic performance, at a static pressure drop, \( \Delta P \neq \Delta P^* \) rectification can also be increased by

\[
\text{FIG. 2.} \text{ (a) Cross-sectional averaged salt concentration } \rho_s(x) \text{ normalized by the bulk concentration } 2\rho_b \text{ as a function of the lateral position } x \text{ for our standard parameter set (see the text). For potential drops, } \Delta \psi = +0.4 \text{ V (red) and } -0.4 \text{ V (blue), for which } \Delta \psi = +31 \text{ mV according to Eq. (6), the solid lines represent concentration profiles at Péclet numbers that vary between } 6 \text{ and } 200 \text{ in steps of } 20. \text{ The green curve represents the case } \Delta \psi = 0 \text{ V at any } \Delta P. (b) The normalized laterally averaged concentration } (\rho_s(x)/2\rho_b) \text{ as a function of the pressure drop } \Delta P \text{ at potential drops } \Delta \psi = +0.4 \text{ V (red), } -0.4 \text{ V (blue), and } 0 \text{ V (green). The solid lines represent Eq. (4), data points are from numerical solutions to the full PNP equations, which for } \Delta \psi = +0.4 \text{ V show an extremum very close to } \Delta P^* = +13 \text{ mbar from Eq. (6) where } \Delta P = 0, \text{ denoted by the vertical dashed lines.}
\]

\[
\Delta P^* = \varepsilon \psi_0 \frac{b (R_i^2 + R_o R_i + R_t^2) R_o}{3 R_t R_i^2} \approx 8 \pi \varepsilon \psi_0 \frac{1}{3 R_t^2},
\]

which yields about \(-32 \) mbar/V for our standard parameter set and about \(-27 \) mbar/V for the extremely large tip-base ratios \( R_t \gg R_i \) generated by the extrusion of a pipette in the experiments of Ref. 46 (if we assume \( \psi_0 = -40 \) mV common for silica\(^{68,69} \)). Clearly, the inverse square scaling of \( \Delta P^* \) with \( R_i \) is key to explaining the dramatic pressure-sensitivity observed in the experiments.\(^{68,69} \) In fact, our results suggest even more pressure-sensitivity for larger conical channels, e.g., for \( R_i = 10 \) m, we have \( \Delta P^* \) in the microbar regime, which can already be exerted by the sound of passing traffic\(^{68,69} \). For cases where \( \Delta P \gg \Delta P^* \), concentration polarization is washed out by the flow; variation of current with both pressure and voltage then closely follows Ohmic conduction. As flow suppresses diodic performance, at a static pressure drop, \( \Delta P \neq \Delta P^* \) rectification can also be increased by lowering the dielectric constant \( \varepsilon \) or increasing the viscosity \( \eta \) thereby lowering the electro-osmotic flow rate while keeping \( \Delta \rho \) unchanged.

Now that we have established that Eq. (4) gives a fair account of the salt concentration profile in the channel, we will use it to approximate \( \rho_w^* \). In the thin-EDL limit, the total current \( I \) is dominated by the conductive component \(-(\varepsilon_{\mathbf{k}B}/T)\rho_s(x, r)\partial_x \psi(x, r)\) of \( x \cdot \partial_x (x, r) \) and cross-sectional integration of this current with Eq. (2) and the same thin-EDL limit as before yields \( I_{\text{cond}}(x) = \pi R_t \rho_s \partial_x \psi(x) / (\varepsilon_{\mathbf{k}B} T L) \), which manifestly depends on \( x \) on the basis of Eq. (4). In steady state, this lateral variation of the conductive

\[
\text{FIG. 3.} \text{ (a) Heat map of the laterally averaged salt concentration } (\rho_w^*) \text{ for the standard parameter set (see the text) in the potential drop } \Delta \psi--\text{pressure drop } \Delta P \text{ plane. (b) Current–pressure } (I–\Delta P) \text{ relation for three fixed potential drops showing a minimum close to } \Delta P = \Delta P^* \text{ of Eq. (6). The symbols represent numerical solutions to the full PNP equations at parameter combinations shown in (a) and the solid lines represent our analytic solution based on Eq. (4). (c) Current–voltage } (I–\Delta \psi) \text{ relation for } \Delta P = 0 \text{ (pink) and the optimal pressure drop } \Delta P = \Delta P^* \text{ (black) which shows increased current rectification ICR compared to } \Delta P = 0. \text{ The inset shows the pressure drop dependence of the ICR=−(l−V))/(l(V), which exhibits two maxima at } \Delta P = \pm \Delta P^* \text{.}
\]
current must be compensated by diffusive and advective currents and the resulting laterally invariant current $I$ can be obtained by treating the concentration profile $\bar{\rho}_i(x)$ as a collection of resistors in series, such that $L_{22} = (D^2/\kappa_b T)\bar{\rho}_i$, which reveals that conductance is proportional to the laterally averaged salt concentration.

For our standard parameter set, we plot $\bar{\rho}_i$ in Fig. 3(a) as a heat map in the $(\Delta \rho, \Delta P)$ plane, including a few iso-concentration contours. We clearly see the largest concentration variations, and hence the largest variations of $L_{22}$, along the black line that represents $\Delta P = \Delta P^*$ of Eq. (6). In Fig. 3(b), we plot the $\Delta P$-dependence of the electric current $I$ (lines) as predicted from Eq. (1) for three voltage drops ($\pm 0.4$ V and zero), together with full numerical calculations (symbols) at the state points indicated by the color-matching symbols in Figs. 3(a), 3(b), and 3(b). The overall agreement is quantitative at $\Delta \rho = 0$, which is fully in the linear-response regime, while the nonlinear gross features at $\Delta \rho = \pm 0.4$ V, especially at $\Delta P \approx \pm \Delta P^* \approx \mp 13$ mbar, are accounted for with reasonable accuracy, the more so at the positive potential drop. In Fig. 3(c), we plot current–voltage relations at pressure drops $\Delta P = 0$ and $\Delta P = \Delta P^*$, using the same color coding as in Fig. 3(a). The degree of non-Ohmic behavior, characterized by the ionic current rectification $I_{CR} = -I(-1V)/I(1V)$, is clearly larger at the optimal pressure drop $\Delta P^*$, which is indeed borne out by the inset which shows the full $\Delta P$ dependence of $I_{CR}$, revealing peaks at $\pm \Delta P^*$.

Finally, using our explicit knowledge of $\bar{\rho}_i(x)$ and the full transport matrix of Eq. (1), we can explicitly search for an optimal cone geometry at which the deviation from Ohmic conductance is largest. Naively, Eq. (5) suggests that for a large concentration profile the ideal tip-to-base ratio should be small ($R_t/R_b \ll 1$); however, Eq. (4) shows that in this limit the concentration profile becomes localized near the tip resulting in a small channel-averaged concentration change. The ideal pore geometry balances the magnitude and spread of the concentration profile and in part (III) of the supplementary material, we show that this optimum occurs at a universal tip-to-base ratio $R_t/R_b \approx 0.22$ for $|\text{Pe}| \leq 1$. The optimum ratio for concentration polarization decreases as the power law $b|\text{Pe}|^{\nu-\nu_0}$ with $b = 2.5$ and $\nu = 0.9$ for $|\text{Pe}| > 10^2$ and $b = 0.9$ and $\nu = 0.55$ for $\text{Pe} \leq 10^2$; for all flow rates, the ideal tip-to-base ratio is less than 0.22. Interestingly, the ideal pore geometry is independent of the channel length $L$, which follows from our Eq. (4) for $\bar{\rho}_i(x)$ that only depends on $x/L$, such that $L_{22}$ (and in fact the whole matrix $L$) is independent of the channel length. Hence the concentration polarization does not depend on the cone opening angle, which is surprising as most authors identify it as the key geometric parameter controlling pressure-sensitivity$^{\text{39,76}}$ and current rectification.

In conclusion, we provide a full microscopic understanding of the ultra-sensitive pressure and voltage dependence of the electric conductivity of cone-shaped channels. We identify and quantify concentration polarization due to geometric frustration which leads to a source term in Eq. (3), even in the thin-EDL case considered here. Moreover, we found an optimal channel geometry $R_t/R_b \approx 0.22$ and an optimal operation condition Eq. (6) for current rectification. These insights are important for further developments of mecanotronic$^{\text{34,47}}$ and biochemical$^{\text{13,31}}$ sensing as well as microfluidic$^{\text{34}}$ and neuromorphic applications.

**SUPPLEMENTARY MATERIAL**

See the supplementary material for (I) the full Poisson–Nernst–Planck–Stokes equations, (II) a detailed derivation of the Onsager matrix $L$, (III) a detailed derivation of the optimal pore geometry, and (IV) a discussion of our full numerical results.

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**AUTHOR DECLARATIONS**

Conflict of Interest

The authors have no conflicts to disclose.

**Author Contributions**

Willem Boon and Tim Veenstra contributed equally to this paper.

**Willem Q. Boon:** Conceptualization (equal); Formal analysis (equal); Investigation (equal); Visualization (lead); Writing – original draft (lead); Writing – review & editing (lead).

**Tim E. Veenstra:** Data curation (lead); Formal analysis (equal); Investigation (equal); Visualization (supporting); Writing – original draft (supporting).

**Marjolein Dijkstra:** Funding acquisition (lead); Project administration (lead); Supervision (lead); Writing – review & editing (equal).

**Rene van Roij:** Funding acquisition (lead); Project administration (lead); Supervision (lead); Writing – review & editing (equal).

**DATA AVAILABILITY**

The data that support the findings of this study are available within the article and its supplementary material.

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