

## Supplementary material: theoretical analysis

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### 1. THEORETICAL DESCRIPTION OF THE SALT DYNAMICS AND RANGE OF OPERATION

#### 1.1. Advection-diffusion equation for the salt

In order to predict the variations of the channel ionic resistance with time, we follow the framework proposed by Taylor and Aris<sup>1-3</sup> to analyze our results. We consider here a channel of radius  $R$ , length  $L$ , and the diffusion coefficient of the salt in the solution is  $D$ . Solving the Navier-Stokes equation for a cylindrical channel, under the assumption of no-slip boundary condition, the velocity profile reads:

$$v(r) = \frac{\Delta P}{4\eta L}(R^2 - r^2) \quad (1)$$

and the average velocity is accordingly:

$$\bar{V} = \frac{1}{\pi R^2} \int_0^R 2\pi r v(r) dr = \frac{\Delta P R^2}{8\eta L}. \quad (2)$$

At  $t = 0$ , a concentration profile  $c(r, t, z)$  is released in the flow. It reads  $c(z \leq 0, t = 0) = c_1$  and  $c(z > 0, t = 0) = c_2$ .

The concentration profile is governed by the advection-diffusion equation which in cylindrical coordinates takes the form:

$$\frac{\partial c}{\partial t} + v(r) \frac{\partial c}{\partial z} = D \left( \frac{\partial^2 c}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) \right) \quad (3)$$

This equation is complemented by the no-flux boundary condition at the channel's surface,  $\frac{\partial c}{\partial r} = 0$  for  $r = R$ . Following Taylor-Aris framework<sup>1,2</sup>, we perform a cross-sectional average over the radial variables. If we consider that the diffusion is fast in the  $r$  direction ( $t \gg R^2/D$ ), so that the concentration is homogeneous in the channel cross-section, then the averaged advection-diffusion

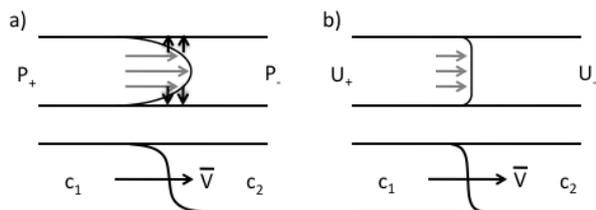


FIG. 1: Sketch of the salt front moving under (a) a pressure driven flow; (b) electro-osmotic flow.

reads:

$$\frac{\partial \bar{c}}{\partial t} + \bar{V} \frac{\partial \bar{c}}{\partial z} = D \left( 1 + \frac{R^2 \bar{V}^2}{48 D^2} \right) \frac{\partial^2 \bar{c}}{\partial z^2} \quad (4)$$

An effective diffusion coefficient  $D_{\text{eff}} = D(1 + \frac{1}{48} Pe^2)$  is introduced, with  $Pe = \frac{R\bar{V}}{D}$  a Peclet number written in terms of the channel lateral size. Note that for a flat slit channel, the Peclet number is defined in terms of the smallest size  $h$  and the numerical prefactor  $1/48$  is changed to  $1/210$ <sup>1-3</sup>.

Accordingly, the concentration profile only depends on the variable  $x = (z - \bar{V}t)/\sqrt{t}$ :  $c = f(x = \frac{z - \bar{V}t}{\sqrt{t}})$ . In this variable, the diffusion-advection equation reduces to  $-\frac{1}{2}x f'(x) = D_{\text{eff}} f''(x)$ , with solution - for our initial conditions -:

$$c(z, t) = \frac{c_1 - c_2}{2} \text{Erf} \left( \frac{z - \bar{V}t}{\sqrt{4D_{\text{eff}}t}} \right) + \frac{c_1 + c_2}{2} \quad (5)$$

with  $\text{Erf}(x) = 2/\sqrt{\pi} \int_0^x du \exp[-u^2]$ .

From this expression, one may extract the electric resistance of the channel. The latter is related to the local conductivity of the salt solution  $\kappa_{\text{el}} = (\lambda_+ + \lambda_-) c$ ,  $\lambda_{\pm}$  being the conductivity of the charged species and  $c$  the local salt (KCl) concentration.

One may consider that the total electric resistance of the channel,  $R_e$ , is the sum of the resistance over its cross-sections, leading to:

$$R_e(t) = \int_0^L \frac{1}{(\lambda_+ + \lambda_-) c(z, t)} \frac{1}{\pi R^2} dz \quad (6)$$

This equation can be integrated numerically. However, if we consider that diffusion in the  $L$  direction is negligible (i.e.  $t \ll L^2/D_{\text{eff}}$ ), the channel is partly filled with  $c_1$  and  $c_2$ , and their resistance can be added so that:

$$R_e(t) = R_{e,1} \frac{\bar{V}t}{L} + R_{e,2} \frac{L - \bar{V}t}{L} \quad (7)$$

with  $R_{e,1-2}$  being the electrical resistance of the channel filled with salt concentration  $c_{1-2}$ . This result can be derived from the full expression, Eq.(6), as the first term of an expansion in terms of the salt concentration difference between the two sides of the channel. Altogether, using Eq.(6), the time  $\tau$  required for the electric resistance to vary from one value to the other is given by  $\tau = L/\bar{V}$ . As shown in the main text, this result was found to be in quantitative agreement with the experimental results.

### 1.2. Convective limit

While the above description assumes a rapid diffusion of the salt across the channel width, it is instructive to explore the opposite regime, in which salt diffusion is put to zero ( $D = 0$ ). In this case, the salt is convected in its original layer. In a cylindrical channel, the advection velocity is given by the Poiseuille expression in Eq.(1). Assuming that the different fluid layers at various distance to the center  $r$  behave as resistors in parallel, one may expect the global electric resistance of the channel to behave as

$$\frac{1}{R_e(t)} = \frac{1}{\pi R^2} \int_0^R 2\pi r dr \times \frac{1}{R_e(r, t)} \quad (8)$$

with  $R_e(r, t) = R_{e,1} \frac{v(r)t}{L} + R_{e,2} \frac{L-v(r)t}{L}$  the resistance associated with the local velocity field  $v(r)$ . Developing for a small  $\Delta R_e = R_{e,1} - R_{e,2}$  (corresponding to a small salt concentration difference), one gets

$$\frac{1}{R_e(t)} = \frac{1}{R_{e,2}} \times \left( 1 - \frac{\Delta R_e}{R_{e,2}} \times \frac{\bar{V}t}{L} \right) \quad (9)$$

where  $\bar{V}$  is the averaged velocity defined in terms of the flow rate as  $\bar{V} = \frac{1}{\pi R^2} \int_0^R 2\pi r dr v(r)$ .

This shows that in this convective limit also, the transition time needed for the global resistance to reach its final plateau value is again given by  $\tau = L/\bar{V}$ , with  $\bar{V}$  the average velocity in the channel, defined in terms of the flow rate.

### 1.3. Range of operation: critical flow rates and channel aspect ratio.

In this section, we review the assumptions underlying the above analysis, in order to infer the range of operation of the method.

Globally, two main hypothesis have been used. First, in the Taylor-Aris approach, a fast transverse diffusion assumption is made, so that the time of the experiment (i.e.  $\tau \sim L/\bar{V}$ ) should be large compared to the diffusion time in the cross section, i.e.  $\tau \gg R^2/D$ . Defining as above the Peclet number as  $Pe = \frac{\bar{V}R}{D}$  and the *width to length* aspect ratio of the channel  $q = R/L$ , this condition reads :

$$q \times Pe \ll 1 \quad (10)$$

We note however that, as discussed above, the main result for the cross-over time to reach the plateau,  $\tau = L/\bar{V}$  is also recovered in the opposite convective limit (with  $D = 0$ ,  $Pe = \infty$ ), so that this condition is not expected not to be essential for the flux monitoring method to operate. Going beyond the above simple estimates to analyze this time-scale separation condition would require to tackle the problem in its full hydrodynamic and electric complexity.

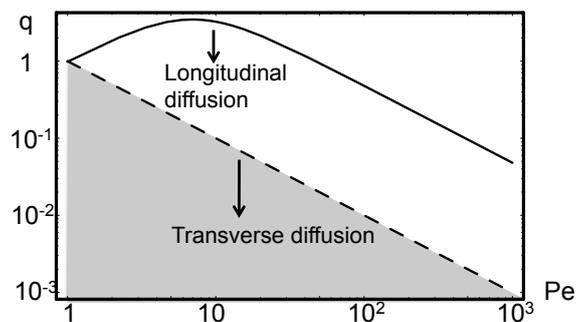


FIG. 2: Range of operation of the flux monitoring method in terms of the Peclet number  $Pe = R\bar{V}/L$  and width-to-length aspect ratio  $q = R/L$  ( $R$  being replaced by the largest width for a shallow microchannel). Lines represent the various conditions for time separation as discussed in the text. The grey zone represents the accessible aspect ratio  $q$  versus  $Pe$  in which the proposed approach is expected to be valid.

Note furthermore that in a shallow channel geometry, say with a height  $h$  and width  $w$  ( $> h$ ), the relevant diffusion time scale was shown by Ajdari *et al.*<sup>3</sup> to be the one associated with the *largest* lengthscale  $w$ , i.e.  $w^2/D$ , so that the above condition is more stringent in this geometry, with the radius  $R$  replaced by the width  $w$  in the above condition in Eq.(10).

A second hypothesis is made implicitly by neglecting diffusion over the length  $L$  of the channel, i.e.  $\tau \ll L^2/D_{\text{eff}}$ , with  $D_{\text{eff}}$  the Taylor-Aris expression for the effective diffusion coefficient. This leads to

$$\frac{Pe}{1 + \alpha Pe^2} \gg q \quad (11)$$

with  $\alpha = 1/48$  or  $\alpha = 1/210$  for channel with cylindrical and slit shape respectively.

Altogether these various criterions define a range of operation for the above results - and the 'flux monitoring' technique - to hold. This domain is sketched in Fig. 2, where we report the accessible width to length aspect ratio as a function of the Peclet number. Note that for  $Pe > 1$ , this second condition in Eq. (11) is actually redundant with the first one in Eq. (10).

The range of operation is very much dependent on the channel width to length aspect ratio. For small width to length ratio, which is quite common for most microfluidics set-ups, both conditions are fulfilled for a very large range of  $Pe$  numbers, making the proposed approach a method of choice to estimate the flow rate and hydrodynamic resistance of the channel. For the  $1\mu\text{m}$  channel considered in the above experiments, the width to length aspect ratio of order  $1.5 \times 10^{-5}$  ensures the validity of the analysis.

We finally quote that in the above description, the external voltage is applied to probe the electric resistance of the channel, while the driving is obtained by the pressure drop. This requires that the EOF induced by the corresponding electric field should be negligible as com-

pared to the flow rate induced by pressure. Using the Smoluchowski expression for the electro-osmotic velocity,  $v_{EO} = \epsilon\zeta\Delta V/(\eta L)^4$ , this condition takes the following form:

$$\delta = \frac{8\epsilon\zeta\Delta V}{R^2\Delta P} \ll 1 \quad (12)$$

with  $\delta$  the ratio between the electroosmotic velocity and flow-rate induced velocity. This condition is filled in most practical situations, as can be verified using typical values. Along the same lines, the streaming currents contribution to the electric current, i.e. ionic current induced in the Debye layer by the pressure driven flow, can be also neglected.

## 2. CHANNELS WITH ARBITRARY SHAPE

The previous description can be used as a simple and versatile diagnostic method to probe the shape of a channel. The general idea is that the time dependent electric resistance is a direct function of the cross-section area  $\mathcal{A}(z)$  of the channel along its length  $z$ . The time dependence of the electric resistance as the salt front travels along the channel is therefore a direct signature of the shape variations.

We rationalize more formally this idea by extending the Taylor-Aris description. Let us consider a channel whose cross section  $\mathcal{A}(z)$  varies along its length  $z$ . For a slowly varying  $\mathcal{A}(z)$ , the Taylor-Aris approach leads to a global cross-over time  $\tau$  now writing:

$$\tau = \int_0^L \frac{dz}{\bar{V}(z)} = \frac{\mathcal{V}_{\text{tot}}}{Q} \quad (13)$$

where we used mass conservation  $Q = \mathcal{A}(z) \times \bar{V}(z) = \text{cst}$ ;  $\mathcal{V}_{\text{tot}} = \int_0^L dz \mathcal{A}(z)$  is the total volume of the channel. This expression can be rewritten in terms of the hydrodynamic resistance of the channel  $\mathcal{R}_{\text{hyd}}$ , defined as

$$\mathcal{R}_{\text{hyd}} = \int_0^L \frac{dz}{\mathcal{A}(z)K_{\text{hyd}}(z)} \quad (14)$$

with  $K_{\text{hyd}}(z)$  the local hydrodynamic permeability, defined as above as  $\bar{V}(z) = K_{\text{hyd}}(z)(-\nabla P)(z)$ . We have accordingly

$$\tau = \frac{\mathcal{V}_{\text{tot}}\mathcal{R}_{\text{hyd}}}{|\Delta P|} \quad (15)$$

Now, while these quantities concern the global properties of the channel over its entire length, much insight can be obtained by monitoring the time-dependence of the

measured electric resistance  $R_e(t)$ . In a quasi-stationary regime, the change in electric resistance over a time interval  $dt$  is obtained by replacing the ion concentration  $c_2$  by  $c_1$  in a volume of length  $\bar{V}(z_t) \times dt = Q/\mathcal{A}(z_t) \times dt$  and cross section  $\mathcal{A}(z_t)$ , so that one gets

$$\frac{dR_e}{dt} = \frac{1}{\bar{\lambda}}\Delta\left(\frac{1}{c}\right) \times \frac{Q}{\mathcal{A}(z_t)^2} \quad (16)$$

with  $\Delta(1/c) = 1/c_2 - 1/c_1$  and  $\bar{\lambda} = \lambda_+ + \lambda_-$ . Here  $z_t = z(t)$  is the position of the salt front at a time  $t$ : it is defined implicitly by the differential equation

$$dt = \frac{dz}{\bar{V}(z)} = \frac{1}{Q}\mathcal{A}(z)dz \quad (17)$$

This shows that variations in the channel cross section  $\mathcal{A}(z)$  lead to changes in the local slope of the time-dependent resistance: a curvature in the electric signal for  $R_e(t)$  is expected to reflect a varying cross-section in the channel. We quote however that this simple description implicitly assumes that the salt concentration is homogeneous over the section of the channel, so that these results do not take into account the transient dynamics associated with this process. This condition imposes that the diffusion time over the change in lateral cross section  $\Delta\mathcal{A}$ , typically  $\tau_{\text{lat}} \sim \Delta\mathcal{A}/D$  should be smaller than the convective time along the channel  $\Delta z/\bar{V}(z)$ . This imposes that a variational Peclet number defined as  $\tilde{P}e = (d\mathcal{A}/dz)\bar{V}(z)/D$  should be much smaller than unity. This suggests that the method is not suited to probe strong variations in the cross section. Finally, we remark that in principle the analysis proposed may be pushed further to reconstruct the full  $z$ -dependent cross section of the channel. Indeed, according to the previous analysis, the measurement allows to formally access both the time-dependence of the cross-area  $\mathcal{A}(t)$ , as well as the velocity at which the channel is explored,  $z(t)$ :

$$\begin{aligned} \mathcal{A}(t) &= \frac{\gamma}{\sqrt{\frac{dR_e}{dt}}} \\ z(t) &= \frac{Q}{\gamma} \int_0^t dt' \times \sqrt{\frac{dR_e}{dt}}(t') \end{aligned} \quad (18)$$

with  $\gamma$  a numerical prefactor defined as  $\gamma = \sqrt{Q \times \bar{\lambda}^{-1} \Delta(1/c)}$ . This shows that a parametric plot allows to reconstruct the profile shape  $\mathcal{A}(z)$  versus  $z$  along the channel. To be quantitative, the reconstruction requires to know the flow rate  $Q$ , and here the problem is somewhat reversed with respect to the previous considerations, as the knowledge of  $Q$  allows to extract the information on the profile  $\mathcal{A}(z)$ .

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