

VI. Electrokinetics

Lecture 31: Electrokinetic Energy Conversion

Notes by MIT Student (and MZB)

1 Linear Electrokinetic Phenomena in a Nanochannel or Pore

1.1 General Theory

We have the following equation for the linear electrokinetic response of a nanochannel:

$$\begin{pmatrix} Q \\ I \end{pmatrix} = \begin{pmatrix} K_P & K_{EO} \\ K_{EO} & K_E \end{pmatrix} \begin{pmatrix} \Delta P \\ \Delta V \end{pmatrix}$$

The basic idea¹ is to apply ΔP and to try to “harvest” the streaming current I or streaming voltage ΔV .

Open-circuit Potential (Streaming Voltage)

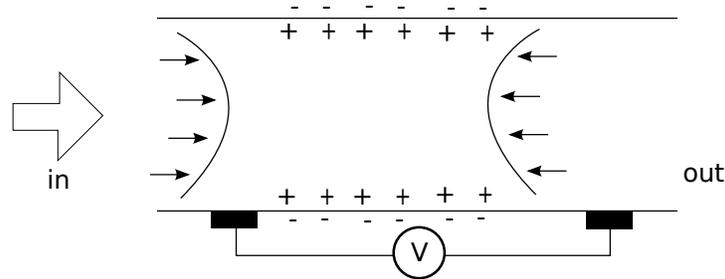
$$I = K_{EO}\Delta P + K_E\Delta V$$
$$I = 0 \Rightarrow \Delta V_O = -\frac{K_{EO}}{K_E}\Delta P$$

Where $K_{EO}\Delta P$ is the streaming current and $K_E\Delta V$ is the Ohmic current.

¹J.F. Osterle, A unified treatment of the thermodynamics of steady state energy conversion, Appl. Sci. Res. 12 (1964), pp. 425-434.

J.F. Osterle, Electro-kinetic energy conversion, J. Appl. Mech. 31 (1964), pp. 161-164.

The same idea was also discovered by Quincke in the 1800s.



$$\Delta P = P_{\text{in}} - P_{\text{out}}$$

$$\Delta V_O = V_{\text{in}} - V_{\text{out}}$$

Then

$$\begin{aligned} Q &= K_P \Delta P + K_{EO} \Delta V \\ &= K_P \left(1 - \frac{K_{EO}^2}{K_P K_E} \right) \Delta P \\ &= (1 - \alpha) K_P \Delta P \\ &= \frac{\det \mathbf{K}}{K_E} \Delta P \end{aligned}$$

where we define $\alpha = \frac{K_{EO}^2}{K_P K_E}$. For a neutral liquid, the response is purely hydraulic ($K_{EO} = 0, \alpha = 0$). For an electrolyte in a charge porous medium (e.g. water in a porous rock or soil) we generally have $\alpha > 0$, so the effective hydraulic conductance $K_P^{eff} = (1 - \alpha) K_P$ is reduced compared to purely pressure-driven flow is reduced by electro-osmotic back flow. Net flow appears to be ≤ 0 (opposite to the applied pressure) when $\alpha \geq 1$, but we now show that this is not possible.

1.1.1 Second Law of Thermodynamics

The energy dissipation or work done on system to drive motion per time (power input) is:

$$\begin{aligned} P &= Q \Delta P + I \Delta V &> 0 \\ &= (\Delta P \Delta V) \mathbf{K} \begin{pmatrix} \Delta P \\ \Delta V \end{pmatrix} &> 0 \end{aligned}$$

P must be positive since irreversible work produces heat in the system.

Since this inequality must hold for any $\Delta P, \Delta V$, the electrokinetic conductance tensor \mathbf{K} is **positive definite**. Therefore its determinant is positive,

$$\det \mathbf{K} = K_P K_E - K_{EO}^2 > 0$$

and $\alpha < 1$.

So, as expected, we can't apply pressure and get a flow in the reverse direction! ($Q = (1 - \alpha)K_P \Delta P$).

1.1.2 Streaming Current Harvesting

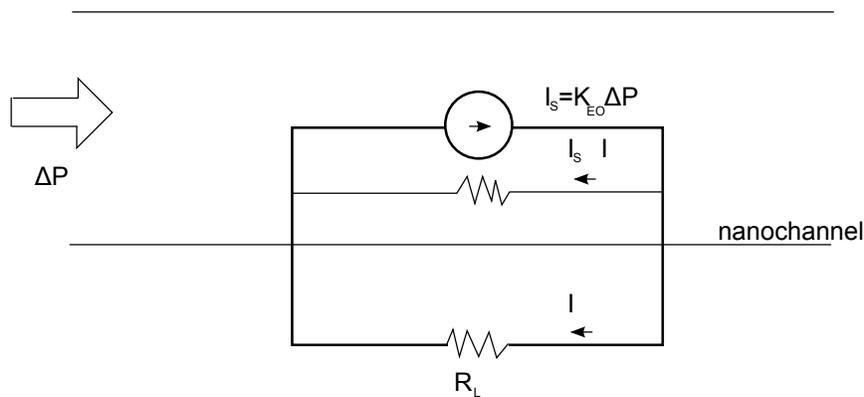
Consider harvesting the streaming current via two electrodes connected by a total load resistance $R_L (= R_{\text{external}} + R_{\text{internal}}$ from interfaces). Then $\Delta V = -IR_L$. Also:

$$\begin{aligned} I &= K_{EO} \Delta P + K_E \Delta V \\ &= K_{EO} \Delta P - K_E R_L I \\ &= \left(\frac{K_{EO}}{1 + K_E R_L} \right) \Delta P \end{aligned}$$

Let $\theta = K_E R_L = \frac{R_L}{R_E} = \frac{\text{external load}}{\text{internal resistance}}$. So:

$$I = \frac{K_{EO} \Delta P}{1 + \theta}$$

So, applied pressure leads to a current source via streaming current, which flows through internal and external resistors in parallel. We have the equivalent circuit:



$$\begin{aligned}
 Q &= K_P \Delta P + K_{EO} \Delta V \\
 &= K_P \Delta P - \frac{K_{EO}^2 R_L \Delta V}{1 + \theta} \\
 &= K_P \Delta P \left(1 - \frac{\alpha \theta}{1 + \theta} \right) \\
 &= K_P \Delta P \left(\frac{1 + \theta - \alpha \theta}{1 + \theta} \right)
 \end{aligned}$$

Efficiency

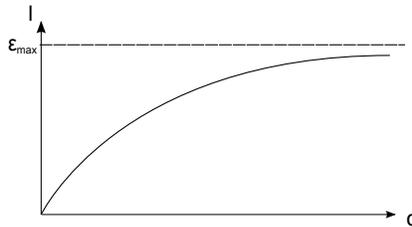
$$\begin{aligned}
 \varepsilon_{EK} &= \frac{P_{\text{out}}}{P_{\text{in}}} = \frac{-I \Delta V}{Q \Delta P} = \frac{I^2 R_L}{Q \Delta P} \\
 &= \frac{\left(\frac{K_{EO} \Delta P}{1 + \theta} \right)^2 R_L}{K_P \Delta P^2 \frac{1 + \theta - \alpha \theta}{1 + \theta}} = \frac{\alpha \theta}{(1 + \theta)(1 + \theta - \alpha \theta)} = \varepsilon_{EK}
 \end{aligned}$$

This efficiency of electrokinetic energy conversion $\varepsilon_{EK}(\theta)$ has a maximum of

$$\varepsilon_{\text{max}} = \frac{\alpha}{\alpha + 2(\sqrt{1 - \alpha} + 1 - \alpha)} \sim \frac{\alpha}{4} \quad \text{for } \alpha \ll 1$$

for specific external load given by

$$\theta_{\text{max}} = \frac{1}{\sqrt{1 - \alpha}}$$



Since $\alpha < 1$ and $\theta_{\text{max}} > 1$, we see that the external load must exceed the internal Ohmic electrical resistance of the pore $R_L > R_E = \frac{1}{K_E}$ for optimal energy efficiency. The same results apply to the efficiency of **electro-osmotic pumping** through an external fluidic resistance $R_P = \frac{1}{K_P}$.

2 Porous Media

Porous or composite materials are useful to “scale up” microfluidic phenomena to macroscopic volumes and useful flow rates. We will discuss general theories of

transport in porous media later in the class. For now, we just need some basic concepts to facilitate our discussion of electrokinetic energy conversion, using porous media or microchannels.

First, define the porosity ϵ_p as the ratio of the volume of pores to the total volume of the system:

$$\epsilon_p = \frac{\text{Pore Volume}}{\text{Total Volume}}$$

Similarly we can define a measure of the pore wall area density as:

$$a_p = \frac{\text{Pore Surface Area}}{\text{Total Volume}}$$

Now consider how to define a mean pore size, h_p . It is clear that

$$h_p = \frac{\epsilon_p}{a_p}$$

has the correct dimensions, lets consider the case of cylindrical pores to confirm that it is a reasonable approximation. For cylindrical pores:

$$\epsilon_p = \pi r_p^2 L$$

$$a_p = 2\pi r_p L$$

$$h_p = \frac{r_p}{2}$$

so we conclude that h_p is a good measure of the mean pore size. The last parameter we will define is the tortuosity τ , which measures how much longer is the mean distance L_p between two points traveling through the pores compared to the straight line distance L between them:

$$\tau = \frac{L_p}{L}$$

3 Linear Electrokinetics: Scaling Analysis

First we will consider a simple scaling analysis of the electrokinetic behavior of a pore as sketched in Figure 1. As discussed in the previous lecture we can relate the flow rate Q , and current I , to the applied pressure and voltage differences ΔP , ΔV through the conductance tensor \mathbf{K} by:

$$\mathbf{K} = \begin{pmatrix} K_p & K_{eo} \\ K_{sc} & K_e \end{pmatrix} \quad (1)$$

Additionally, from Onsager's symmetry principle we know that \mathbf{K} must be a symmetric matrix so $K_{sc} = K_{eo}$. In order to perform our scaling analysis we will develop approximate expressions for each of the components of \mathbf{K} .

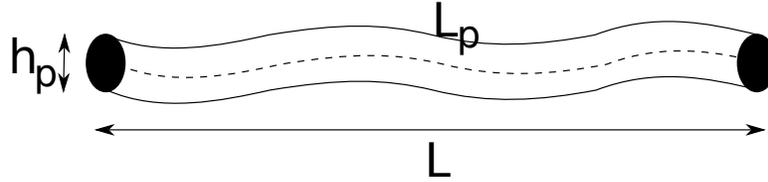


Figure 1: Sketch of an example pore.

3.1 Hydraulic Conductance

An estimate of the hydraulic conductance K_p is given by:

$$K_p \sim \frac{h_p^2}{L_p} k_p$$

where k_p is given by:

$$k_p \sim \frac{h_p^2}{\eta}$$

plugging this in gives the scaling of K_p as:

$$K_p \sim \frac{h_p^4}{\eta L_p} \quad (2)$$

3.2 Electrical Conductance

In general a scaling estimate of K_e is given by:

$$K_e \sim \frac{h_p^2}{L_p} k_e \quad (3)$$

where k_e is the electrical conductance of the material in the pore. We will consider two limits of k_e corresponding to the thin double layer, small surface charge regime and the thick double layer, large surface charge regime.

3.2.1 Thin Double Layers ($\epsilon = \frac{\lambda_d}{h_p} \ll 1$)

In this limit the conductance of the bulk electrolyte dominates the conductance of the double layer giving:

$$k_e \sim k_e^{\text{bulk}} \sim \frac{De^2c_0}{k_bT} \sim \frac{D\epsilon}{\lambda_d^2} \quad (4)$$

3.2.2 Thick Double Layers

In the limit of thick double layers and large surface charge the pore is filled almost entirely with counter ions and they dominate the electrical conductance. Since we know that the counterions will balance out the surface charge on the pore wall we have:

$$k_e \sim \frac{De}{k_b T} \frac{|q_s|}{h_p} \quad (5)$$

Now plugging in Equations 4 and 5 back in to Equation 3 we obtain the scaling of the electrical conductance in each limit:

$$K_e \sim \begin{cases} \frac{De}{L_p} \frac{h_p^2}{\lambda_d^2}, & \text{thin double layers or low charge} \\ \frac{De|q_s|h_p}{k_b T L_p}, & \text{thick double layer, large charge} \end{cases} \quad (6)$$

3.3 Electroosmotic Conductance

As for the electrical conductance we will estimate the electroosmotic conductance in the limits of thin and thick double layers. First, the electroosmotic conductance is given generally by:

$$K_{eo} \sim \frac{\epsilon}{\eta L_p} \int_{A_{typ}} dx dy (\zeta - \psi) \quad (7)$$

3.3.1 Thin Double Layers

In the limit of thin double layers $\psi = 0$ over most of the area of the pore so the integral reduces to ζh_p^2 giving:

$$K_{eo} \sim \frac{\epsilon}{\eta L_p} \zeta h_p^2$$

Since we are more interested in the case of constant surface charge than constant zeta potential we use the relation

$$\zeta \sim \frac{q_s \lambda_d}{\epsilon}$$

to obtain:

$$K_{eo} \sim \frac{h_p^2}{\eta L_p} q_s \lambda_d \quad (8)$$

3.3.2 Thick Double Layers

For the case of thick double layers we estimate the order of magnitude of $(\zeta - \psi)$ from the capacitance of the pore giving:

$$(\zeta - \psi) \sim \frac{q_s}{C_{pore}} \sim \frac{q_s h_p}{\epsilon}$$

plugging this in to Equation 7 yields:

$$K_{eo} \sim \frac{q_s h_p^3}{\eta L_p} \quad (9)$$

3.4 Energy Conversion Efficiency

Now that we have scaling estimates for each component of \mathbf{K} we will estimate the maximum efficiency that can be obtained from an electrokinetic device using the relation

$$\epsilon_{max} \sim \frac{K_{eo}^2}{K_p K_e} \quad (10)$$

derived last lecture for the limit of low efficiencies. By substituting the values of K_{eo} , K_p , and K_e from Equations 9, 8, 2, 6 we get the scaling estimate for ϵ_{max} in the two limits of interest:

$$\epsilon_{max} \sim \begin{cases} \frac{q_s^2 \lambda_d^4}{\eta \epsilon D h_p^2}, & \text{thin double layers or low charge} \\ \frac{|q_s| k_B T}{\eta D e} h_p, & \text{thick double layers, large charge} \end{cases} \quad (11)$$

It is important to note here that ϵ_{max} scales as $1/h_p^2$ for the thin double layer case, and as h_p in the thick double layer case. Since the thick double layer case corresponds to small mean pore sizes this means that the efficiency increases with pore size in the small pore limit, but decreases with pore size for large pores. Therefore there must be a maximum efficiency that occurs for intermediate pore sizes on the order of λ_d , this effect is depicted in Figure 2. Recent work has predicted that efficiencies over 10% are theoretically possible, and efficiencies close to 1.4% have been demonstrated, as shown in the Figure.

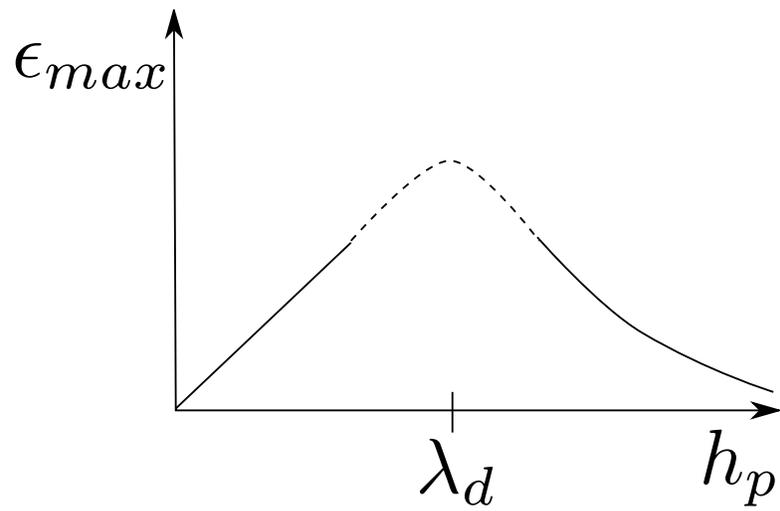


Figure 2: Scaling of the maximum efficiency with pore size

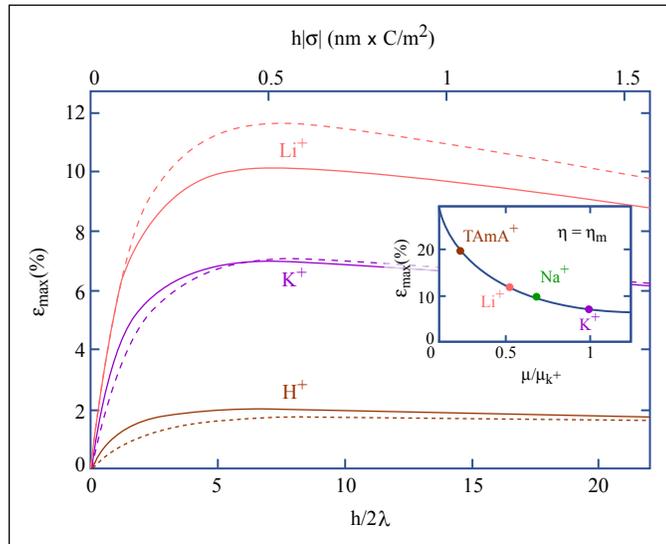


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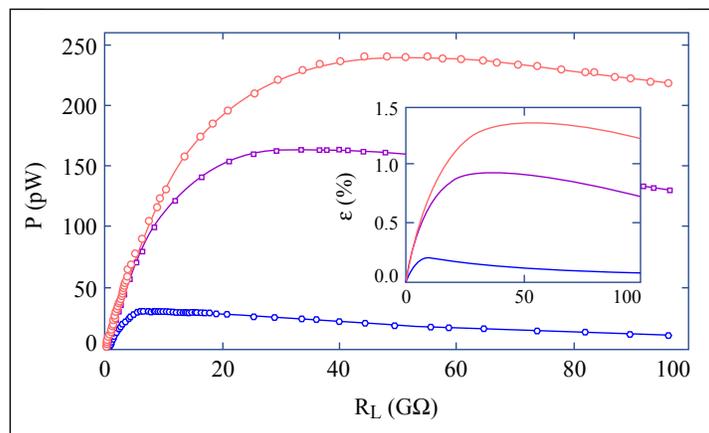


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Figure 3: Top: theoretical efficiency of electrokinetic energy conversion versus channel thickness [van der Heyden et al. (2006)]. Bottom: Experimental results for a 500nm deep silica nanochannel at different reservoir KCl concentrations [van der Heyden et al (2007)].

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