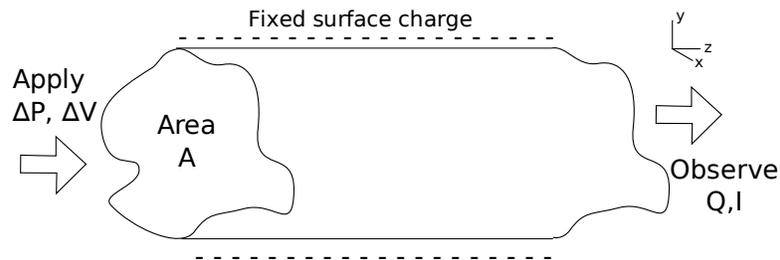


## VI. Electrokinetics

### Lecture 30: Linear Electrokinetic Phenomena

Notes by MIT Student (and MZB)

#### 1 Linear Electrokinetic Resonse of a Nanochannel



We start with the system in equilibrium

$$\begin{aligned}
 Q &= 0 \\
 I &= 0 \\
 \varepsilon \nabla^2 \psi &= \rho(\psi) \\
 \nabla p_E &= -\rho_{eq} \nabla \psi
 \end{aligned}$$

Where  $p_e$  is the electrostatic pressure.

Now, consider applying a small perturbation  $\Delta P$ ,  $\Delta V$  and calculate linear response, and assume diffuse charge does not change:

$$\begin{aligned}
 \phi(x, y, z) &= \underbrace{\psi(x, y)}_{\text{equilibrium potential profile}} - \underbrace{E_0 z \hat{z}}_{\text{small perturbation: axial electric field}} \\
 p(x, y, z) &= p_E(x, y) - G_0 z \hat{z} \\
 \nabla p &= -\nabla_{\perp} p_E + \underbrace{G_0 \hat{z}}_{\text{small}}
 \end{aligned}$$

The transverse gradient  $\nabla_{\perp} = \frac{\partial}{\partial x}\hat{x} + \frac{\partial}{\partial y}\hat{y}$ . The Poisson equation is now:

$$\rho = -\varepsilon\nabla^2\phi = -\varepsilon\nabla_{\perp}^2\psi = \rho_{eq}(\psi)$$

The full PDES:

$$\begin{aligned}\rho &= -\varepsilon\nabla^2\phi \\ \nabla p &= \eta\nabla^2\vec{u} + \rho\vec{E}\end{aligned}$$

reduce to

$$\begin{aligned}\rho_{eq}(\psi) &= -\varepsilon\nabla_{\perp}^2\psi \\ -G_0 &= \eta\nabla_{\perp}^2\vec{u} - \varepsilon(\nabla_{\perp}^2\psi)E_0\end{aligned}$$

Let  $u = u_E + u_p$ ; the velocity has electrosmotic and pressure driven components, where:

$$-G_0 = \eta\nabla_{\perp}^2\vec{u}_p \quad (1)$$

$$\varepsilon(\nabla_{\perp}^2\psi)E_0 = \eta\nabla_{\perp}^2\vec{u}_E \quad (2)$$

To solve this, we have

$$\vec{u}_E = \frac{\varepsilon(\psi - \varphi)}{\eta}E_0$$

where we introduce an another harmonic function,  $\nabla_{\perp}^2\varphi = 0$  which satisfies  $\varphi = \psi$  on the boundary (no slip). For a symmetric cross section (e.g. parallel plates or a cylindrical pore), the potential of the surface is constant by symmetry, so  $\varphi = \zeta = \text{constant}$  (since the unique solution of Laplace's equation with constant Dirichlet boundary condition is a constant function).

### 1.1 Pressure driven flow

$$Q_p = \int_A u_p dx dy \equiv Ak_p G_0$$

where  $k_p$  is hydrodynamic permeability, eg  $k_p = \frac{h^2}{12\eta}$  for parallel plates. Alternatively,

$$Q_p = K_p \Delta P$$

where

$$\begin{aligned}G_0 &= -\frac{\Delta P}{L} \\ K_p &= \frac{Ak_p}{L}\end{aligned}$$

## 1.2 Electrical current

$$\begin{aligned} I_E &= \int_A \sigma E_0 dx dy \\ &= Ak_E E_0 = K_E \Delta V \end{aligned}$$

where

$$\sigma(\psi) = \text{axial conductivity} = \frac{e^2}{k_B T} (z_+^2 D_+ c_+(\psi) + z_-^2 D_- c_-(\psi))$$

for a binary electrolyte, and  $c_{\pm}$  = equilibrium ion profiles.

## 1.3 Electro-osmotic flow

$$\begin{aligned} Q_E &= \int_A u_E dx dy \\ &= \frac{\varepsilon}{\eta} E_0 \int_A (\psi - \varphi) dx dy \\ &\equiv Ak_{EO} E_0 \\ &= K_{EO} \Delta V \end{aligned}$$

where

$$\begin{aligned} K_{EO} &= \frac{\varepsilon}{\eta L} \int_A (\psi - \varphi) dx dy \\ E_0 &= \frac{-\Delta V}{L} \\ K_{EO} &= \frac{Ak_{EO}}{L} \end{aligned}$$

## 1.4 Streaming current

$$\begin{aligned}
 I_p &= \int_A \rho u_p dx dy \\
 &= -\varepsilon \int_A (\nabla_{\perp}^2 \psi) u_p dx dy \\
 &= -\varepsilon \int_A (\nabla_{\perp}^2 (\psi - \varphi)) u_p dx dy \\
 &= -\varepsilon \int_A (\psi - \varphi) \nabla_{\perp}^2 u_p dx dy \\
 &= -\frac{\varepsilon}{\eta} \int_A (\psi - \varphi) G_0 dx dy \\
 &\equiv A k_{SC} G_0 \\
 &= K_{SC} \Delta P
 \end{aligned}$$

In the fourth line, we make use of the identity,  $\int (\nabla^2 f) g dx dy = \int f (\nabla^2 g) dx dy$  if  $f$  and  $g$  vanish on the boundary<sup>1</sup>, which is the case for the pressure driven flow  $u_p$  and the electro-osmotic flow  $u_e \sim \psi - \varphi$ .

Thus we have that

$$K_{SC} = K_{EO} \quad (\text{Onsager relation})$$

This result is very general, for any charge distribution  $\rho_e(\psi)$  and any cross-sectional geometry.

## 2 General Linear Electrokinetics

For any small disturbance (linear), the driving forces and resulting fluxes can be expressed as:

$$\begin{pmatrix} \text{fluxes} \end{pmatrix} = \begin{pmatrix} \text{symmetric} \\ \text{matrix} \\ \mathbf{K} = \mathbf{K}^T \end{pmatrix} \begin{pmatrix} \text{gradients} \\ \text{thermodynamic} \\ \text{forces} \end{pmatrix}$$

<sup>1</sup>Proof: For volume  $V$  and surface  $S$ ,  $\int_V (\nabla^2 f) g dV = \int_V (\nabla \cdot (g \nabla f) - \nabla f \cdot \nabla g) dV = \oint_S \hat{n} \cdot (g \nabla f) dS - \int_V \nabla f \cdot \nabla g dV$  (divergence theorem)  $= \oint_S \hat{n} \cdot (g \nabla f - f \nabla g) dS + \int_V f \nabla^2 g dV$ . The surface integral vanishes if  $f$  and  $g$  vanish on the boundary. This is a generalization of integration by parts.

Specifically, for a nanochannel,

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

With the Onsager relations  $\mathbf{K} = \mathbf{K}^T$ . Onsager (1931) derived this relation for linear response of a general system near thermal equilibrium, assuming local, microscopic time reversibility of the equations of motion. Here we see it emerge explicitly for linear electrokinetic response in a nanochannel.

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