VI. Electrokinetics

Lecture 30  Linear Electrokinetic Phenomena

MIT Student

1 Linear Electrokinetic Response of a Nanochannel

We start with the system in equilibrium

\[ Q = 0 \]
\[ I = 0 \]
\[ \varepsilon \nabla^2 \psi = \rho(\psi) \]
\[ \nabla p_E = -\rho_{eq} \nabla \psi \]

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:

\[
\phi(x, y, z) = \frac{\psi(x, y)}{\text{equilibrium potential profile}} - \frac{E_0 z \hat{z}}{\text{small perturbation: axial electric field}}
\]

\[
p(x, y, z) = p_E(x, y) - G_0 z \hat{z}
\]

\[
\nabla p = -\nabla_{\perp} p_E + G_0 z \hat{z}
\]

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

\[
\rho = -\varepsilon \nabla^2 \phi = -\varepsilon \nabla^2 \psi = \rho_{eq}(\psi)
\]

The full PDES:

\[
\rho = -\varepsilon \nabla^2 \phi \\
\nabla p = \eta \nabla^2 \vec{u} + \rho \vec{E}
\]

reduce to

\[
\rho_{eq}(\psi) = -\varepsilon \nabla^2_\perp \psi \\
-G_0 = \eta \nabla^2_\perp \vec{u} - \varepsilon (\nabla^2_\perp \psi) \vec{E}_0
\]

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

\[
-G_0 = \eta \nabla^2_\perp \vec{u}_p \\
\varepsilon (\nabla^2_\perp \psi) \vec{E}_0 = \eta \nabla^2_\perp \vec{u}_E
\]

To solve this, we have

\[
\vec{u}_E = \frac{\varepsilon (\psi - \varphi)}{\eta} \vec{E}_0
\]

where we introduce an another harmonic function, \( \nabla^2_\perp \varphi = 0 \) 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 \( \varphi = \zeta = \) constant (since the unique solution of Laplace’s equation with constant Dirichlet boundary condition is a constant function).

### 1.1 Pressure driven flow

\[
Q_p = \int_A u_p dxdy \equiv Ak_p G_0
\]

where \( k_p \) is hydrodynam permeability, eg \( k_p = \frac{u^2}{12\eta} \) for parallel plates. Alternatively,

\[
Q_p = K_p \Delta P
\]

where

\[
G_0 = \frac{-\Delta P}{L} \\
K_p = \frac{Ak_p}{L}
\]
1.2 Electrical current

\[ I_E = \int_A \sigma E_0 dx dy \]
\[ = A k_E E_0 = K_E \Delta V \]

where

\[ \sigma(\psi) = \text{axial conductivity} = \frac{e^2}{k_BT} \left( z_+^2 D_+ c_+(\psi) + z_-^2 D_- c_-(\psi) \right) \]

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

1.3 Electro-osmotic flow

\[ Q_E = \int_A u_E dx dy \]
\[ = \frac{\varepsilon E_0}{\eta} \int_A (\psi - \varphi) dx dy \]
\[ \equiv A k_{EO} E_0 \]
\[ = K_{EO} \Delta V \]

where

\[ K_{EO} = \frac{\varepsilon}{\eta L} \int_A (\psi - \varphi) dx dy \]
\[ E_0 = \frac{\Delta V}{L} \]
\[ K_{EO} = \frac{A k_{EO}}{L} \]
1.4 Streaming current

\[ I_p = \int_A \rho u_p dxdy \]
\[ = -\varepsilon \int_A (\nabla_\perp^2 \psi) u_p dxdy \]
\[ = -\varepsilon \int_A (\nabla_\perp^2 (\psi - \varphi)) u_p dxdy \]
\[ = -\varepsilon \int_A (\psi - \varphi) \nabla_\perp^2 u_p dxdy \]
\[ = -\varepsilon \int_A (\psi - \varphi) \nabla_\perp^2 u_p dxdy \]
\[ = -\varepsilon \eta \int_A (\psi - \varphi) G_0 dxdy \]
\[ \equiv A k_{SC} G_0 \]
\[ = K_{SC} \Delta P \]

Thus we have that

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

2 General Linear Electrokinetics

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

\[
\begin{pmatrix}
\text{fluxes}
\end{pmatrix} =
\begin{pmatrix}
\text{symmetric matrix}
\end{pmatrix}
\begin{pmatrix}
\text{thermodynamic forces}
\end{pmatrix}
\]

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 \( K = K^T \). 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.