“Electrokinetics” refers to the study of electrically driven mechanical motion of charged particles or fluids. Sometimes it is used more narrowly for fluid or particle motion in electrolytes and ionic liquids (reserving the term “electrohydrodynamics” for weakly conducting dielectric liquids). Here we examine the basic electrokinetic equations for electrolytes, as well as several types of electrokinetic phenomena.

1. Basic Equations

1.1 Governing equations for flow, concentration, and electrical potential, and key assumptions

A description of an electrokinetic system requires governing equations for the local bulk fluid velocity, local species concentrations \( \{c_i\} \), and (mean) electrical potential \( (\phi) \).

One can obtain concentration profiles from a conservation of mass and electrical potential from electrostatic considerations. These concepts are embodied in the Poisson-Nernst-Planck equations. Specifically, the conservation of mass combined with the Nernst-Planck expression for flux yields the mass conservation expression for an ionic species. The Poisson equation expresses the electrostatic phenomena that determine the potential.

For a dilute solution, the Nernst-Planck equation takes the following form:

\[
\frac{\partial c_i}{\partial t} + \mathbf{u} \cdot \nabla c_i = \nabla \cdot \left[ D_i \nabla c_i + D_i z_i c_i \frac{\varepsilon \phi}{k_B T} \right]
\]

The mean field approximation of the electrostatic potential is described by the Poisson equation, which relates the electrical potential to the charge density.

\[
-\nabla \cdot (\varepsilon \nabla \phi) = \rho_e = \sum_{i=1}^{n} z_i c_i
\]

The Navier-Stokes equation (NSE) is an expression of conservation of linear momentum for a Newtonian fluid with constant mass density. Now we allow for fluid motion due to electrostatic force \( \mathbf{F}_e \) by adding a term to the NSE to represent the body force density due to electrostatic force.
\[ \rho_m \left( \frac{\partial \ddot{u}}{\partial t} + \ddot{u} \cdot \nabla \ddot{u} \right) = -\nabla p + \eta \nabla^2 \ddot{u} + \vec{f}_e \]

Where \( \rho_m \) is the mass density of the fluid and \( \vec{f}_e \) is the electrostatic body force density.

The left-hand side of the NSE represents the convective transfer of linear momentum. A source of linear momentum is the divergence of stress \((\eta \nabla^2 \ddot{u})\). The divergence of the stress tensor captures the viscous stress effects.

In addition, the continuity equation for an incompressible fluid reduces to \( \nabla \cdot \ddot{u} = 0 \)

One can express the electrostatic body force density as a function of the mean electrical potential \((\phi)\) using the Poisson equation.

\[ \vec{f}_e = \rho_e \vec{E} = -\rho_e \nabla \phi \]

\[ -\rho_e = \varepsilon \nabla^2 \phi = -e \sum_i z_i c_i \]

\[ \vec{f}_e = (\varepsilon \nabla^2 \phi) \nabla \phi \]

We now simplify the NSE by making the following assumptions:

1.) Neglect unsteady terms (no time derivatives). This is an appropriate assumption unless there is forcing at high frequency. It is justified by comparing the kinematic viscosity to the mass diffusivity. Given \( \nu = \frac{\eta}{\rho_m} \) = kinematic viscosity = diffusivity of vorticity and \( D = \) mass diffusivity, one can assume that the fluid momentum diffuses quickly when \( \nu \gg D \). For example, if the system is in water, the fluid momentum relaxes quickly, so one typically neglects the time derivative of the velocity.

2.) For low Reynold’s number flows, \( \text{Re} = \frac{u_m L}{\nu} \ll 1 \) and one can neglect the inertial term of the NSE.

Now the Navier-Stokes equation reduces to Stokes’ Equation with an extra term. As a result there are two equations to describe the flow: the Stokes’ Equation and continuity.

\[ \rho_m \left( \frac{\partial \ddot{u}}{\partial t} + \ddot{u} \cdot \nabla \ddot{u} \right) = -\nabla p + \eta \nabla^2 \ddot{u} + \vec{f}_e \]

\[ \nabla p = \eta \nabla^2 \ddot{u} + (\varepsilon \nabla^2 \phi) \nabla \phi \]

\[ \nabla \cdot \ddot{u} = 0 \]

A word on quasi-eletroneutrality:

In a quasi-eletroneutral bulk, the charge density is approximately zero. However, there are charges that can put significant force on the fluid, so it is not appropriate to simplify the Poisson equation to LaPlace’s equation, even though the charge density is approximately zero.
1.2 Nondimensionalize the governing equations

We first choose scales for each variable, so that we may redefine the variables in the following way:

\[ \tilde{\nabla} = \hat{l} \nabla \]
\[ \tilde{\phi} = \frac{\phi}{kT} \quad \text{or} \quad \tilde{\phi} = \frac{\phi}{\phi_{\text{ref}}} \quad \text{where} \quad \phi_{\text{ref}} = V_{\text{applied}} \]
\[ \tilde{u} = \frac{u}{u_{\text{ref}}} \]
\[ \tilde{p} = \frac{p}{p_{\text{ref}}} \]

Substitution of these dimensionless variables yields a dimensionless form of the Navier-Stokes equation:

\[ \tilde{\nabla} \tilde{p} = \tilde{\nabla}^2 \tilde{u} + (\tilde{\nabla}^2 \tilde{\phi})(\tilde{\nabla} \tilde{\phi}) \]

The reference velocity is not determined by the physical dimensions of the system, but rather is a result of a dominant balance. The dominant balance allows us to express \( u_{\text{ref}} \) in terms of physical parameters.

One possible dominant balance is the balance between the viscous and the electrostatic terms. This balance answers the following question: “If I have charges in the system, what is the biggest velocity I could get from the movement of those charges?” The result is called the electroviscous velocity.

\[ \eta \nabla^2 \tilde{u} \sim \rho_e \nabla \tilde{\phi} \]
\[ \eta \frac{u_{\text{ref}}}{L^2} \sim \left( \epsilon \frac{e_{\text{ref}}}{L} \right) \left( \frac{kT}{e} \right) \]
\[ u_{\text{ref}} = \frac{c_{\text{ref}} k TL}{\eta} \]

If the charge density is rescaled via the Poisson equation, one can arrive at an equivalent expression for the reference velocity.
Another possible dominant balance is the balance between the pressure and the electrostatic terms. The result is the dynamic pressure that balances the electrostatic energy density. In other words, the dynamical pressure responds to the electrical pressure.

\[ p_{\text{ref}} = \varepsilon \left( \frac{kT}{e} \right) \]

\[ \eta u_{\text{ref}} \sim \varepsilon \left( \frac{kT}{e} \right) \left( \frac{kT}{e} \right) \]

\[ u_{\text{ref}} = \frac{\varepsilon \left( kT^2 \right)}{\eta L} \]

Another possible dominant balance is the balance between the pressure and the electrostatic terms. The result is the dynamic pressure that balances the electrostatic energy density. In other words, the dynamical pressure responds to the electrical pressure.

\[ p_{\text{ref}} = \varepsilon \left( \frac{kT^2}{e} \right) \]

\[ p_{\text{ref}} = \varepsilon \left( \frac{kT^2}{eL} \right) = \varepsilon E_{\text{ref}}^2 \text{ where } E_{\text{ref}} = \frac{kT}{eL} \]

### 2. Bulk electroconvection

Consider a quasi-neutral bulk electrolyte (outside thin double layers). If the ion concentrations (conductivity) are uniform, the Poisson equation reduces to Laplace’s equation.

\[ \varepsilon \nabla^2 \phi = 0 \]

\[ \nabla^2 \phi = 0 \]

There is no electrostatic force on the fluid (at the leading order, as the small parameter \( \varepsilon = \frac{\hat{\lambda}_D}{L} \to 0 \)). The result is that the flow is described by Stokes’ equation for low Reynolds number flow.

If there are concentration gradients, then the Poisson equation does not reduce to Laplace’s equation (meaning \( \nabla^2 \phi \neq 0 \)) due to conductivity variations. This leads to forces on the fluid even in the “neutral” bulk. This phenomenon is called “bulk electroconvection.”

Usually this effect is small unless \( E = -\nabla \phi \) and \( \nabla c \) are large. In the double layer, this force is typically weak compared to other forces in the double layer. However, in the bulk, the force on the fluid is still small but the resistance to flow is also small, so bulk electroconvection can be observed.
3. Electrokinetic phenomena due to diffuse charge

The electrostatic body force is large in the double layers but the proximity of the charged no-slip surface leads to huge viscous drag, so there is also large viscous resistance to flow. The balance of these forces leads to electro-osmotic flow.

![Schematic of double layer and bulk electrolyte](image)

Figure 29.1: Schematic of double layer and bulk electrolyte in a flow system near a charged wall with an applied electric field.

The ions very close to the wall (within the double layer) experience a large electric force, while those ions in the quasi-electroneutral bulk feel a relatively small electric force. An imposed electric field drives a current, which in turn generates flow that looks like a plug flow slipping over the surface. There is an effective slip velocity \( u_s \) observed just outside the double layer.

When there is a constant surface charge, \( u_s \propto E \), one may observe a number of related linear electrokinetic phenomena: electro-osmotic flow, streaming current, streaming potential (described in sections 3.1, 3.2, 3.3). In addition, there are analogous phenomena for freely suspended charged colloidal particles, such as electrophoresis and sedimentation potential (see sections 3.4 and 3.5).

Note that there are also nonlinear “induced-charge” electrokinetic phenomena at polarizable surfaces, such as electrodes, where the surface charge is not constant.

3.1 Electro-osmotic flow

Electro-osmotic flow is flow that is induced by an applied potential or electric field in a system that has an imbalance of charge (for example, by having charged walls). Namely, one applies a potential \( \nabla \phi \), or \( E = -\frac{\Delta \phi}{L} \) and the result is approximately a plug flow with slip velocity \( u_s \).
that is a function of $E$. That is, the flow velocity is proportional to the gradient in potential, and therefore proportional to the electric field.

![Figure 29.2: Schematic of electro-osmotic flow profile driven by application of a background electric field to fluid in a channel with negatively-charged walls.](image)

### 3.2 Streaming current

The application of a pressure gradient to an incompressible, enclosed fluid results in a Poiseuille flow profile (a parabolic flow profile). The flow then causes a “streaming current”, because the flow carries with it some of the net charge in the system. When you apply a pressure gradient ($\nabla p$, or $G = \nabla p \sim \frac{\Delta p}{L}$) to a system with charged walls, there is a current that is proportional to the pressure gradient. The streaming current can be “harvested” by redox reactions at electrodes or membranes at the ends of the channel (as in Figure 29.3). Streaming current will only occur if the flowing charges have somewhere to go. If it is a closed system, with no net flow of fluid in or out, then the steady state result is a field that generates a reverse flow to balance the flow generated by the pressure gradient. This field is proportional to the “streaming potential” in the system (see Section 3.3)
3.3 Streaming potential

A streaming potential occurs as a result of an applied pressure gradient in a system wherein no current flows because there is no ion source or sink. If no current flows, an electric field \( \frac{\Delta V}{L} = E \) develops to drive electroosmotic flow that opposes or cancels the applied pressure-driven flow.

Figure 29.4: Schematic of streaming potential caused by a pressure gradient applied to a closed system with charged walls. The potential arises to counteract the net flow caused by the mechanical pressure.
3.4 Electrophoresis

The term “electrophoresis” describes the phenomenon in which dispersed (colloidal) particles move relative to a fluid under the influence of a background electric field. The dispersed particles have an electric surface charge and are freely suspended in an electrolyte solution, but the particles themselves do not conduct electricity. The external electric field exerts an electrostatic (Coulombic) force on the particles and on the counter ions in the diffuse double layer. The overall system of the particle and the ions in the double layer is neutral, so there is no net electrostatic body force. Therefore, the particle moves not because of an electric force, but because of the “slipping” motion of the double layer. This is considered “force free” motion. The result is that the particle moves at a velocity proportional to the electric field. The particle “swims” by electro-osmotic flow around it.

![Figure 29.5: Schematic of electrophoresis, the motion of charged colloidal particles due to an applied electric field.](image)

3.5 Sedimentation potential

A sedimentation potential occurs when dispersed particles move relative to the bulk fluid under the force of gravity or centrifugation. As an external force pulls on the particle, the diffuse charge in the double layer is pushed from the “front” (the leading surface) to the back. The separation of the diffuse charge via this flow induces an electric field (a gradient in potential, $\Delta V$).
Figure 29.6: Schematic of the sedimentation potential of a colloidal particle. The motion of the particle as a result of a gravitational body force drives a separation of charge that induces an electric potential gradient.

4. Electro-osmosis

The fundamental phenomenon is electroosmotic slip in a thin double layer.

Figure 29.7: Physical schematic of an electro-osmotic flow profile in a two-dimensional, Cartesian system.

4.1 Governing equation and key assumptions
The Navier-Stokes equation for low Re flow is shown below with a term for the electrostatic body force.
\[ \nabla p = \eta \nabla^2 \bar{u} + (\epsilon \nabla^2 \phi)(\nabla \phi) \]

We now assume the following:

1. The double layer is thin relative to the geometric length scale of the system. The potential drop across the double layer is defined as the difference in potential between the bulk fluid and the no-slip plane.
   \[ \psi_D = \Delta \phi_D = \phi_{x=0} - \phi_{\text{bulk}} = \zeta \]
   The subscript “ \( x = 0 \)” refers to a hypothetical point called the “no-slip” plane or the “shear” plane. This is the position at which the no-slip boundary condition applies. The term “ \( \zeta \)” is the zeta potential.

   The calculation of the zeta potential depends on the model for the double layer. For example, the Debye-Huckel theory asserts that the zeta potential depends on the surface change, the capacitance of the double layer, and the thickness of the double layer.
   \[ \psi_D = \zeta = \frac{q_s}{C_D} \frac{\lambda_D q_s}{\epsilon} \]

2. The flow is unidirectional (in the “x” direction), tangent to a flat, charged plane, and only varies in the normal (“y”) direction.
   \[ \bar{u}(x, y) \sim u_x(y) \hat{x} \]

   For an impermeable wall, \( u_y \ll u_x \), so this assumption is reasonable. Also, the thinness of the double layers implies that the variations in the y-direction (over the span of \( \lambda_D \)) are much greater than the variations in the x-direction (over the span of L) because \( \lambda_D \ll L \), which justifies the assumption that the velocity is a strong function of y.

3. The electrical potential takes the following functional form:
   \[ \phi(x, y) \sim \psi(y) - (Ex) \hat{x} \]
   The term “\( \psi \)” represents the potential variation to diffuse charge, whose composition varies only in the “y” direction. In addition, there is a uniform, background tangential field applied (E) in the “x” direction.

The assumptions are generally valid for thin double layers.

### 4.2 Analysis of the y-component of the Navier-Stokes equation

We now consider the y-component of the Navier-Stokes equation.
\[ \frac{\partial p}{\partial y} = \eta \left( \frac{\partial^2 u_y}{\partial x^2} + \frac{\partial^2 u_y}{\partial y^2} \right) + \left( \epsilon \frac{\partial^2 \phi}{\partial y^2} \right) \left( \frac{\partial \phi}{\partial y} \right) \]
There are no velocity terms because we have assumed the flow is unidirectional.
We now substitute the expression for electric potential and integrate the expression.

\[
\frac{\partial p}{\partial y} = \left( \varepsilon \frac{\partial^2 \psi(y)}{\partial y^2} \right) \frac{\partial \psi(y)}{\partial y}
\]

Integration of this differential equation yields the following expression for pressure as a function of the electric field in the \( y \)-direction.

\[
p = \overline{p} + \frac{1}{2} \varepsilon \left( \frac{\partial \psi}{\partial y} \right)^2 = \overline{p} + \frac{\varepsilon}{2} E_y^2
\]

Note that \( \overline{p} \) is the bulk pressure, and the term \( \frac{1}{2} \varepsilon \left( \frac{\partial \psi}{\partial y} \right)^2 \) is the electrostatic energy density.

### 4.3 Analysis of the \( x \)-component of the Navier-Stokes equation

\[
\frac{\partial p}{\partial x} = \eta \left( \frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_s}{\partial y^2} \right) + \varepsilon \left( \frac{\partial^2 (\psi(y) + Ex)}{\partial x^2} + \frac{\partial^2 (\psi(y) + Ex)}{\partial y^2} \right) \frac{\partial (\psi(y) + Ex)}{\partial x}
\]

\[
\frac{\partial p}{\partial x} = \eta \frac{\partial^2 u_x}{\partial y^2} + \varepsilon \left( 0 + \frac{\partial^2 \psi}{\partial x^2} \right) E
\]

We address the shear stress term by splitting up the velocity in the \( x \)-direction into two terms: one that embodies the velocity effects of the pressure gradient and one that represents the effects of electro-osmotic flow.

\[
u_s = u_p + u_{EO}
\]

\[
\frac{\partial p}{\partial x} = \eta \frac{\partial^2 u_p}{\partial y^2}
\]

\[
\eta \frac{\partial^2 u_{EO}}{\partial y^2} = \varepsilon \left( \frac{\partial^2 \psi}{\partial y^2 \right) E
\]

The velocity term “\( u_p \)” represents flow that balances viscous stresses with mechanical forcing (the applies or self-generated pressure).

The velocity term “\( u_{EO} \)” represents flow that balances viscous stresses with electrical forcing (electro-osmotic flow).

The electro-osmotic flow profile can be obtained by integrating the differential equation relating the electro-osmotic velocity and the potential. We impose boundary conditions at the “no slip” plane \( (y = 0) \) and at points outside the double layer \( (y \to \infty) \).
The second boundary condition states that the potential has a finite value ($\zeta$) at the no-slip plane. The no-slip plane is the plane at which the velocity is zero, but not necessarily the zero plane of the coordinate system.

The most general approach is to obtain $\psi_D(y)$ from a double layer model (such as the Debye-Huckel model or Gouy-Chapman model).

This derivation is very general. It has two key assumptions:
1. A mean field theory
2. The viscosity and permittivity ($\eta$ and $\varepsilon$, respectively) are constant fluid properties.

If these assumptions are appropriate, this electro-osmotic slip formula is valid for any charge distribution, even if it is not an equilibrium charge distribution. That is, the formula is valid for any charge distribution and potential that satisfy the Poisson equation $\rho = -\varepsilon \frac{\partial^2 \psi}{\partial y^2}$.

More generally, the $x$-direction NSE is solved by a dominant balance, and the selection of terms to include in the balance is a function of the physical phenomenon in question. A dominant balance of the shear stress term and the electrostatic term results in an expression for electro-osmotic flow. A dominant balance of the shear stress term and the pressure term results in an expression for streaming potential or streaming current caused by pressure driven flow in small channels.
5. Diffusio-osmosis

In addition to externally applied pressure gradients along the surface (as in streaming current), there can also be spontaneous osmotic pressure gradients due to tangential variations in bulk salt concentration, which lead to an additional fluid flow called “diffusio-osmosis”, which exists in addition to electro-osmosis. The combination of electro and diffusio osmosis in a thin quasi-equilibrium double layer is called “first kind” electro-osmotic slip (while flows that arise when the double layer goes out of equilibrium due to a large, over-limiting current are of the “second kind”, using S. S. Dukhin’s terminology). The motion of charged particles in response to salt concentration gradients is called “diffusiophoresis”, or, if there is also an applied electric field or current, “electrodiffusiophoresis”.

For a thin, quasi-equilibrium double layer in a dilute binary electrolyte (Gouy-Chapman model), the effective first-kind electro-osmotic slip can be expressed as

\[
\bar{u}_x = \frac{\varepsilon}{\eta} \left[ \zeta \frac{\partial \phi}{\partial x} - 4 \left( \frac{k_B T}{z e} \right)^2 \ln \left( \cosh \frac{z e \zeta}{4 k_B T} \right) \frac{\partial \ln c}{\partial x} \right]
\]

where bars indicate bulk variables just outside the diffuse part of the double layer, and x is the tangential direction to the surface as above. The first term is the HS formula for electro-osmotic slip, while the second term is the diffusio-osmotic slip due to a tangential bulk salt concentration gradient. Note that diffusio-osmotic flow is always directed down the concentration gradient, regardless of the sign of the surface charge (or zeta). The derivation follows that above, only one also allows for slow x variation of the bulk ion concentrations, in addition to fast y variation due to diffuse charge screening the surface.

As shown in the figure, diffusio-osmotic flow results from tangential variations in double-layer pressure, which can be understood via the following scaling argument based on the electrokinetic equations above. The fluid (electro-osmotic) pressure balances the electrostatic energy density, primarily due to the normal electric field

\[
p \sim \varepsilon \left( \frac{\partial \phi}{\partial y} \right)^2 \sim \frac{\varepsilon_e^2}{\lambda_D^2} \sim \frac{2(z e \zeta)^2}{k_B T} \bar{c}
\]
The resulting pressure-driven tangential flow comes from a balance of the tangential pressure-gradient and the viscous drag

\[ \eta \frac{\partial^2 u_x}{\partial y^2} \sim \frac{\partial p}{\partial x} \Rightarrow u_x \sim \frac{\lambda_0^2}{\eta} \frac{\partial p}{\partial x} \sim \frac{\varepsilon \xi^2}{\eta \varepsilon} \frac{\partial \varepsilon}{\partial x} \]

which is the same as the general formula above in the Debye-Huckel limit of small zeta, up to the sign, which is negative based on the physical argument in the Figure. (This shows the power of simple scaling arguments yet again!)

### 6. List of variables

- \( \varphi \): electrical potential
- \( c_i \): concentration of species \( i \)
- \( t \): time
- \( D_i \): diffusivity of species \( i \)
- \( \bar{u} \): mean fluid velocity (a vector)
- \( z_i \): valence of species \( i \)
- \( e \): charge of an electron
- \( k_B \): Boltzmann constant
- \( T \): temperature
- \( \varepsilon \): permittivity
- \( \rho_e \): net charge density or electrical charge concentration
- \( \rho_m \): mass density of the bulk fluid
- \( p \): dynamic pressure (includes thermodynamic pressure and gravitational terms)
- \( \eta \): (shear) viscosity
\( \vec{F}_e \)  electrostatic force vector

\( \vec{j}_e \)  electrostatic body force density (a vector)

\( \vec{E}, E \)  electric field vector and magnitude, respectively

\( \nu \)  kinematic viscosity

\( \text{Re} \)  Reynolds number

\( u_{\text{ref}} \)  reference velocity

\( L \)  reference length

\( \phi_{\text{ref}} \)  reference potential

\( c_{\text{ref}} \)  reference concentration

\( E_{\text{ref}} \)  reference electric field magnitude

\( \vec{\nabla}, \nabla^2 \)  dimensionless gradient and LaPlacian operators, respectively

\( \tilde{\phi} \)  dimensionless potential

\( \tilde{u} \)  dimensionless velocity

\( \tilde{p} \)  dimensionless pressure

\( V_{\text{applied}} \)  applied electric potential drop

\( \psi_D \)  potential drop across the double layer (from the no slip plane to the bulk fluid)

\( \zeta \)  zeta potential

\( q_s \)  wall charge density

\( \lambda_D \)  Debye length; thickness of the double layer

\( C_D \)  capacitance of the double layer

\( u_s, u_y \)  component of the velocity vector in the x-direction and y-direction, respectively

\( u_P, u_{\text{EO}} \)  component of the velocity vector due to pressure-driven flow and electro-osmotic flow, respectively

\( u_s \)  (electro-osmotic) slip velocity