Because of the net free charge in the diffuse layer, if you apply a tangential electric field you get motion! This is called <u>electroosmosis</u> and is <u>very</u> useful in µfluidic systems.

First, what is the free charge density $\rho^{(f)}$? Recall that we had the Boltzmann distribution:

$$n^K = n_b^K e^{-\left(\frac{e z^K \psi}{kT}\right)}$$

we <u>defined</u> $\Psi = \frac{e z \psi}{kT}$

$$so \quad n^K = n_b^K e^{-\Psi \left(\frac{z^K}{z}\right)} \quad \overleftarrow{\quad} \begin{array}{l} +1 \text{ or } -1 \\ dep. \text{ on } + \text{ or } - \\ \quad charge \end{array}$$

That's because, say, positive ions are attracted to a negative surface & neg. ions are repelled!

Suppose we have a $z-z$ electrolyte where the bulk concentration of each is n_b

(They have to be the same for electro-neutrality). The net free charge is:

$$\rho^{(f)} = e \sum n^k z^k = e n_b z \left(e^{-\bar{\Psi}} - e^{+\bar{\Psi}} \right)$$

$\uparrow$ pos. ions $\uparrow$ neg. ions

For 1-1 electrolytes, $z = 1$

We also had, for some surface potential $\bar{\Psi}_s$:

$$\bar{\Psi} = 2 \ln \left(\frac{1 + e^{-\kappa x} \tanh \left(\frac{1}{4} \bar{\Psi}_s \right)}{1 - e^{-\kappa x} \tanh \left(\frac{1}{4} \bar{\Psi}_s \right)} \right)$$

so $e^{-\bar{\Psi}} = \left(\frac{1 - e^{-\kappa x} \tanh \left(\frac{1}{4} \bar{\Psi}_s \right)}{1 + e^{-\kappa x} \tanh \left(\frac{1}{4} \bar{\Psi}_s \right)} \right)^2$

and $e^{\bar{\Psi}}$ is just the inverse.

It is convenient (but not necessary!) to work w/ the low $\bar{\Psi}_s$ limit:

$$\bar{\Psi} \approx \bar{\Psi}_s e^{-\kappa x}$$

and so $\rho^{(f)} = -2 e n_b z \sinh(\bar{\Psi})$

$$\approx -2 e n_b z \bar{\Psi}_s e^{-\kappa x}$$

If we recall that $K^{-1} = \left(\dfrac{\varepsilon \varepsilon_0 kT}{2e^2 z^2 n_b} \right)^{1/2}$

we can recast this as:

$$\rho^{(f)} \approx -\varepsilon \varepsilon_0 K^2 \psi_s e^{-Kx}$$

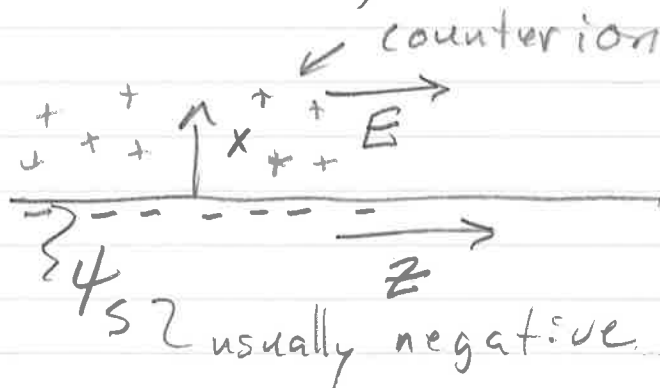or, as usually written,

$$\rho^{(f)} = -\varepsilon \varepsilon_0 K^2 \zeta e^{-Kx}$$

$\hookrightarrow$ known as the Zeta potential

The ζ zeta potential is known as the potential at the <u>shearing surface</u>, but for small ψ_s it is just ψ_s — for <u>large</u> potentials there is a "bound" Stern layer of counter-ions that have <u>low mobility</u>.

OK, now we apply a <u>tangential field</u> E.

ζ usually negative

There is a force per volume on the fluid:

$$0 = \mu \frac{\partial^2 u_z}{\partial x^2} + \rho^{(f)} E$$

so:

$$\frac{\partial^2 u_z}{\partial x^2} = - \frac{\rho^{(f)} E}{\mu} = \frac{\varepsilon \varepsilon_0 K^2 \zeta}{\mu} e^{-Kx} E$$

Let's scale:

$$x^* = Kx \qquad u_z^* = \frac{u_z}{U_c}$$

$$\therefore \quad K^2 U_c \frac{\partial^2 u_z^*}{\partial x^{*2}} = E \frac{\varepsilon \varepsilon_0 K^2}{\mu} \zeta e^{-x^*}$$

$$\therefore \quad U_c = \left(\frac{\varepsilon \varepsilon_0 \zeta}{\mu} \right) E$$

and

$$\frac{\partial^2 u_z^*}{\partial x^{*2}} = e^{-x^*}$$

Integrating once:

$$\frac{\partial u_z^*}{\partial x^*} = -e^{-x^*} + C_1$$

At __infinity__ the stress is __zero__, so $C_1 = 0$,

Integrating again:

$$u_z^* = e^{-x^*} + C_2$$

but $u_z^*\big|_{x^*=0} = 0$ (no-slip) $\therefore C_2 = -1$

so $u_z^* = e^{-x^*} - 1$

Far away (but remember how short K^{-1} is!)

$$\underline{u_z^* = -1}$$

So our electroosmotic velocity is just $-U_0$!

The quantity $\dfrac{\varepsilon \varepsilon_0 \xi}{\mu}$ is the electroosmotic mobility. Note that this is independent of n_b! It only depends on ξ and fluid properties! why? If n_b increases, so does $\xi^{(f)}$ but since K^{-1} decreases viscous drag (which goes as K^2) cancels this out!

So what is $\mu_{eo} \equiv \dfrac{\varepsilon \varepsilon_0 \zeta}{\mu} \equiv$ electro osmotic mobility?

We can plug in some numbers!

Say $\zeta = 100\,mV$ (typical value)

$\mu = 10^{-3}\,Pa\cdot s$ (or $1\,cp$) and $\varepsilon = 80$ (water)

This yields:

$$\mu_{eo} = 7.08 \times 10^{-8}\,\frac{m/s}{V/m}$$

The more usual units are:

$$\mu_{eo} = 7.08\,\frac{\mu m/s}{V/cm}$$

as microfluidic channels are pretty short!

This is a good approx provided ζ_s isn't too big. For larger values, just integrate the exact solution numerically!

   EO velocities are small, but they are very useful for driving fluid through thin channels! For pressure driven flow

The velocity goes as $\underline{depth}^2$. $\boxed{39}$ That means that for, say, $50\mu m$ deep channels you need a <u>large</u> ΔP! For EO the velocity is <u>indep</u> of <u>depth</u>.

    Another advantage — there's no <u>shear</u> as you get <u>plug</u> <u>flow</u> – essentially slip at the walls! For a <u>straight</u> <u>channel</u> there's <u>no</u> <u>Dispersion</u>!

    Now for disadvantage: For a large aspect ratio channel <u>curves</u> are <u>huge</u> sources of dispersion due to the "race track effect":

focused band

dispersed band

$\overset{\longleftrightarrow}{W}$
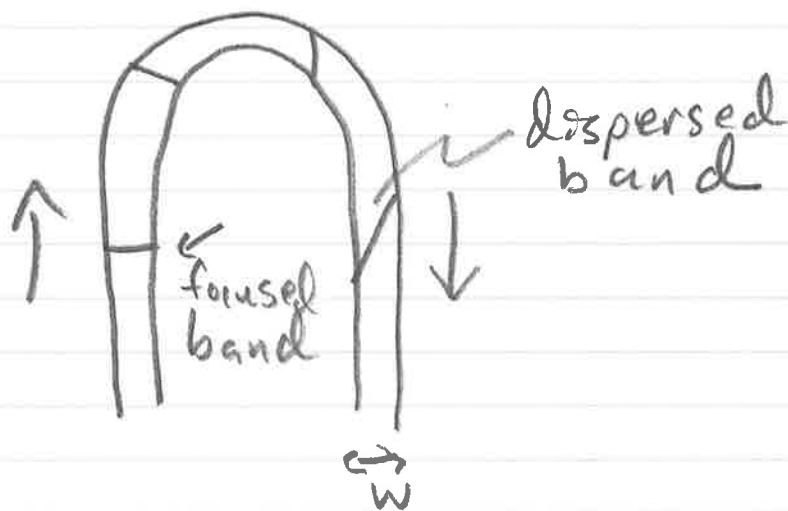
The explanation is simple: The <u>inside</u> of the 180° bend is πW shorter than the <u>outside</u>. This means a <u>higher</u> <u>electric field</u> and a <u>shorter distance</u>. A focused band smears out by $2\pi W$ after <u>every</u> bend, which <u>really</u> adds up on a serpentine channel (needed for length). <u>Modifications</u> to the width profile can reduce this, but it's still a problem!

Another issue is the <u>generation</u> of the electric field. To get <u>any</u> field beyond K^{-1} thickness (<u>really</u> short) you <u>have to have</u> a current! That means an <u>electrode reaction</u> at each end! This is <u>usually</u> producing electrolysis, acid & base (pH change) and bubbles —

all of which cause trouble!

A last disadvantage: If you have a slug of mixed solutes, the electric field will separate them. This can be undesirable, but is actually the basis of capillary electrophoresis, our next topic!

Suppose we have a particle of radius a and surface charge Q. If $\kappa a \ll 1$ (e.g. really small particle or a low n_b) then the diffuse layer is spread out! If we apply an electric field E_∞ then the force is just $E_\infty Q$. This is balanced by Stokes Law drag:

$$E_\infty Q = 6\pi \mu a u$$

The electrophoretic mobility of the particle is:

$$\mu_{ep} = \frac{Q}{6\pi\mu a} \quad ; \quad u = \mu_{ep} E_\infty$$

For a _thin_ double layer $\kappa a \gg 1$ and we have a more complicated result. Essentially, you get EO flow at the _surface_ of the particle (in the double layer) and the particle moves in the opposite direction of this!

we get:

$$u = \frac{Q}{4\pi\mu a} \frac{1}{\kappa a} E_\infty$$

or, in terms of the ζ potential:

$$u = \frac{\varepsilon \varepsilon_0 \zeta}{\mu} E_\infty$$

which is _indep_ of a as $\frac{Q}{4\pi a^2}$ is the _charge density_

Because of this, mobilities in an electric field are used to <u>measure</u> the ζ potential of colloids.

So how is this used in capillary electrophoresis? A mixture of analytes (pos or neg charge!) are drawn through the capillary by <u>electroosmosis</u>: The EO velocity needs to be <u>higher</u> than the neg. vel of opposite charge species. Species w/ different charge <u>or</u> size move w/ dif. velocities and separate into bands for detection at the end of the capillary.

A key is initial focusing of the band at injection using stacking: If you suspend the analyte in a low conc. buffer at the entrance it will <u>focus</u> at the

lead edge due to a higher electric field in the initial slug (low conductivity = high field for same current).

Other tricks are things like iso-electric focusing: The charge on a protein depends on the pH. If you put it in an axial pH gradient it will focus at its isoelectric point (pH of neutral charge) and be convected along w/ the EO velocity. Many other variations have also been developed!

Another way the diffuse layer, EO and electrophoresis can combine is if you also have a shear flow in the absence of an imposed electric field. This leads to a streaming potential.

Consider:


$u_z = \dot{\gamma} x$

Imposed flow
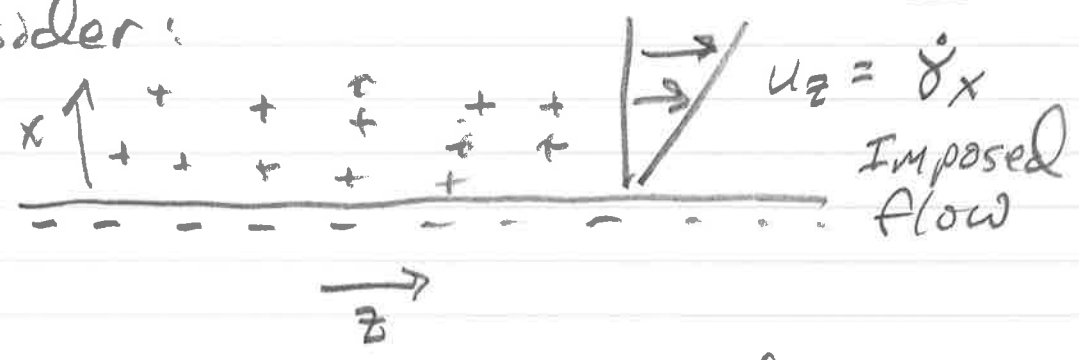
If there's <u>no</u> electric field the positive counter ions are swept along with the shear flow. This net <u>current</u> will (like a Van de Graaf generator) lead to a charge buildup! The current scales as

$$(\kappa^{-1}\dot{\gamma})\,\kappa^{-1}\cdot W \cdot \rho^{(f)}$$

char. velocity   length   extension in to paper   aug. free charge

Since it goes as $(\kappa^{-1})^2$ it is <u>most</u> important for large κ^{-1} (<u>low</u> ion conc. in the bulk) and is quite a problem in pumping gasoline! Ground your pipes to avoid sparks!

    This is <u>also</u> important for charged pores in membranes.
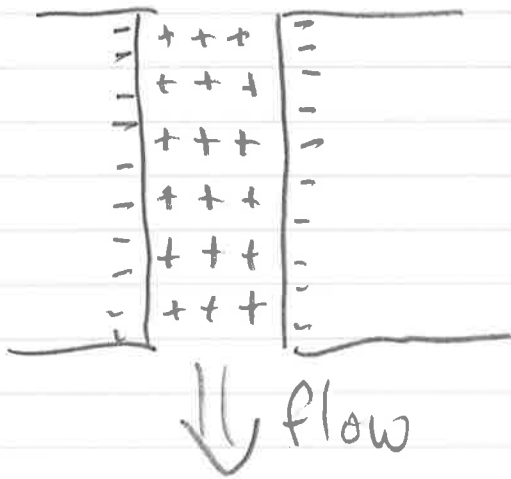
↓ flow

If the pore radius is comparable to K^{-1} pressure driven flow leads to a <u>net convection</u> of counter ions <u>across</u> the membrane. By overall electro neutrality this leads to a membrane <u>polarization</u> and EO flow back the other way!

Polarization can also occur if a membrane is permeable to <u>some</u> ions but not others — Diffusion alone can lead to a <u>Donnan</u> <u>potential</u> — which is how your nerves work! Electrokinetics is a <u>huge</u> subject! This is just an <u>introduction</u>!