Traveling-Wave Electroosmosis:
Faradaic currents and diffusion layer

ELECTROHIDRODINÁMICA Y MEDIOS GRANULARES COHESIVOS

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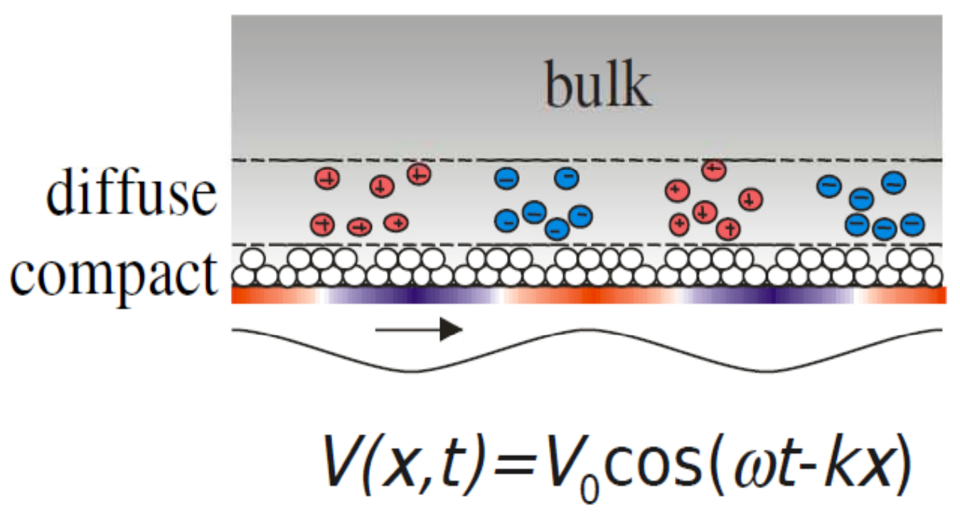
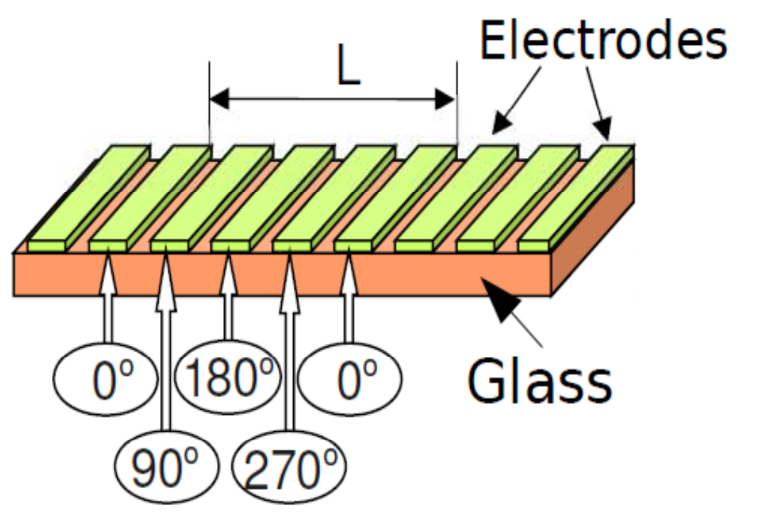
Introduction

- AC electroosmosis can be used for pumping electrolytes in microsystems. We use microelectrodes subjected to Traveling-Wave (TW) potentials (*see figure*)
- For voltages above a threshold, the flow direction is reversed. We perform experiments to elucidate the physical origin of the *flow reversal* and propose that *Faradaic currents and changes in pH* have to be taken into account.
- We also extend the linear model of AC electrosmosis: the two ionic species have different mobilities and one of them can undergo Electrochemical Reactions.
The model for the Electrical Double Layer is extended and the *diffusion layer* is considered. Flow in the reverse direction is predicted under specific circumstances.

Traveling-Wave Potentials



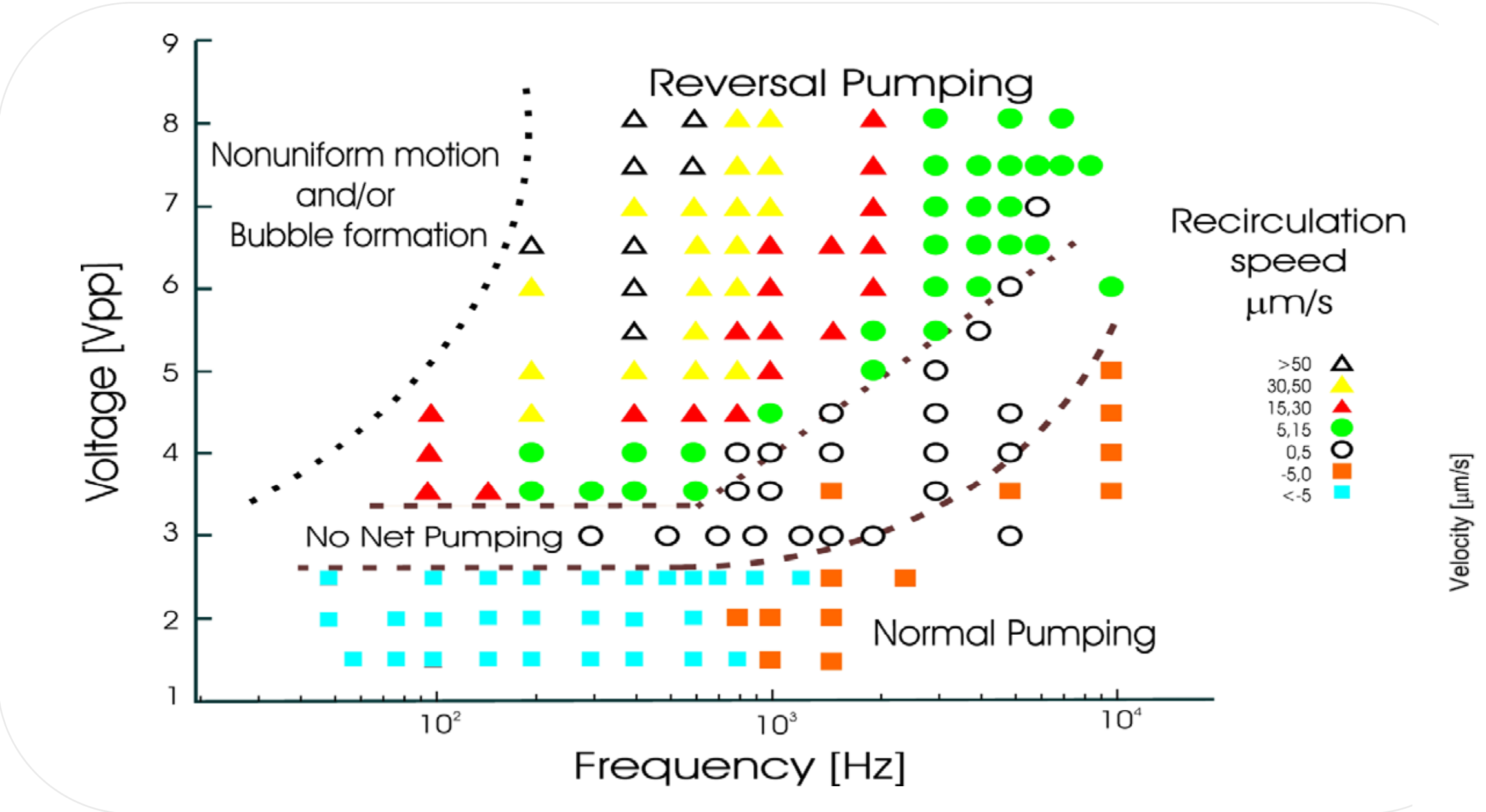
a) Counterions are accumulated at the interface and pulled in the direction of the TW driving the fluid

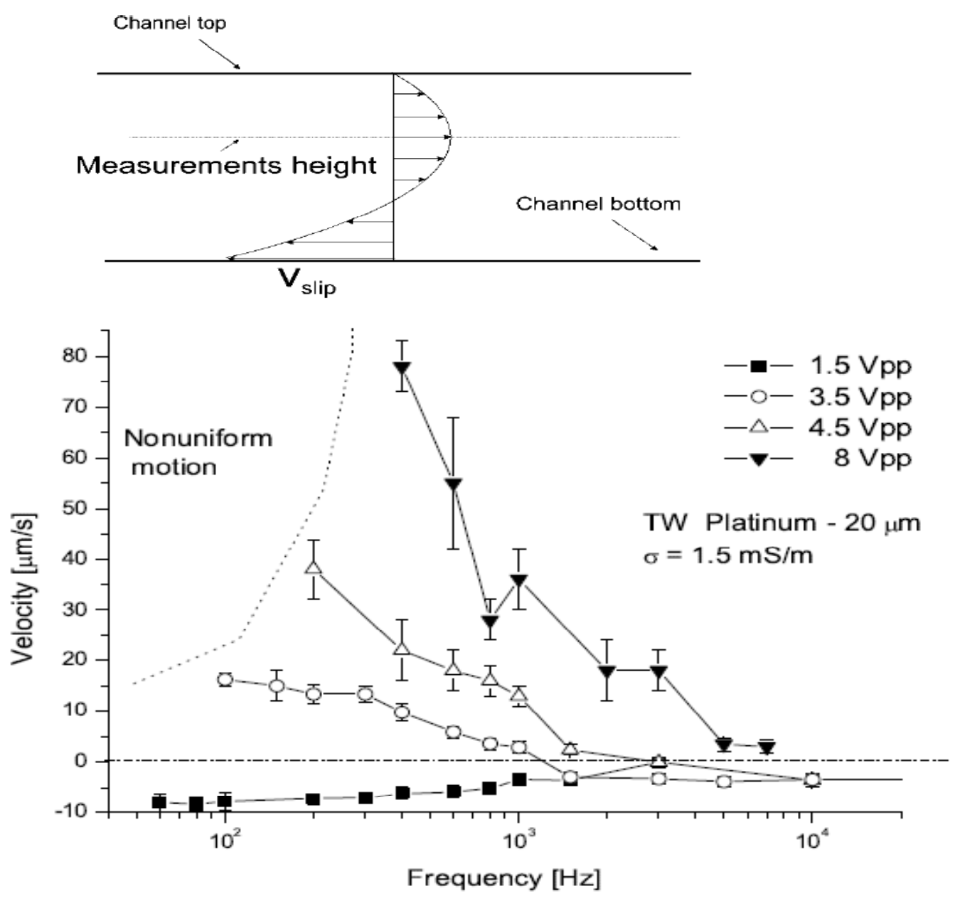


b) In experiments, we apply a TW signal of four phases on a planar array of microelectrodes

Fluid Flow Measurements

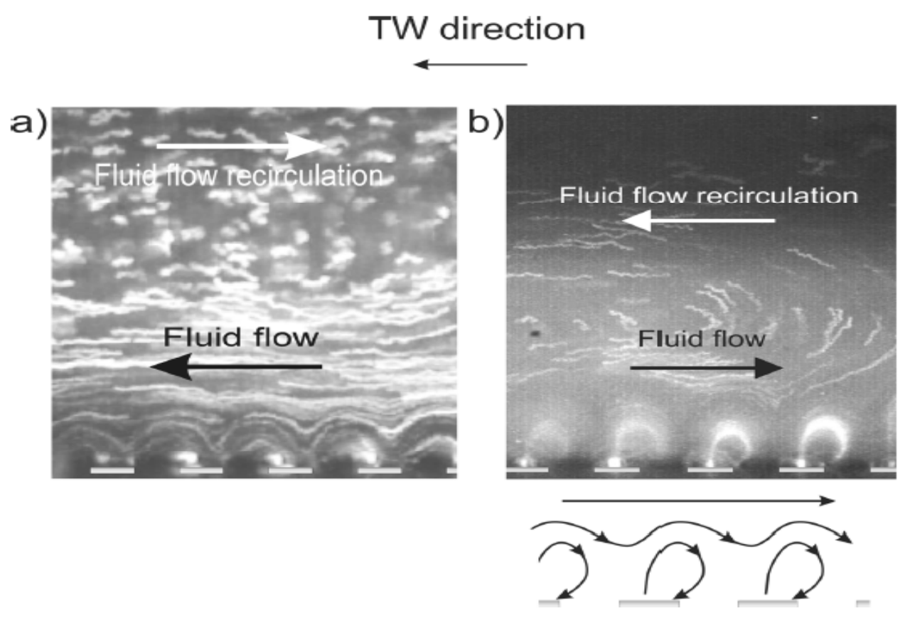
Array of electrodes of Platinum (20 μm width) with an aqueous solution of KCl (1.5 mS/m) .
We made a closed microfluidic channel and measured the recirculation velocity





For low amplitudes of the AC signals, the liquid moves in the expected direction (*Normal Pumping*).
Above 3.5 V_{pp}, flow in the reverse direction occurs (*Reverse Pumping*).

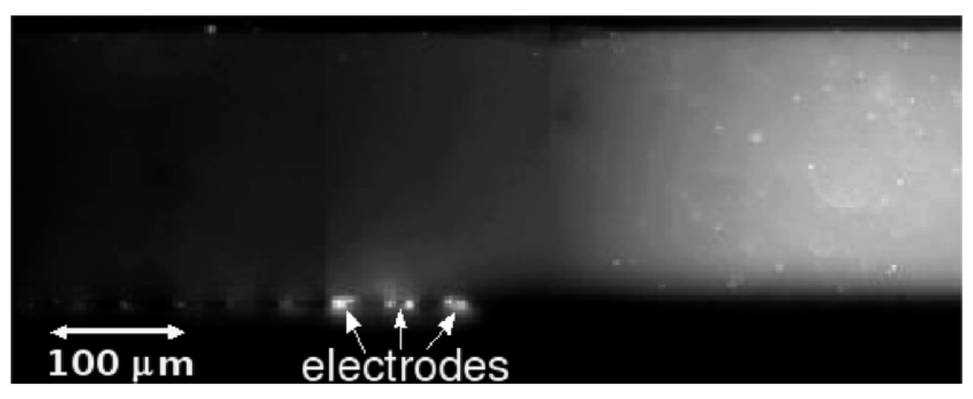
Streamlines



Normal Pumping Reverse Pumping

Changes in pH

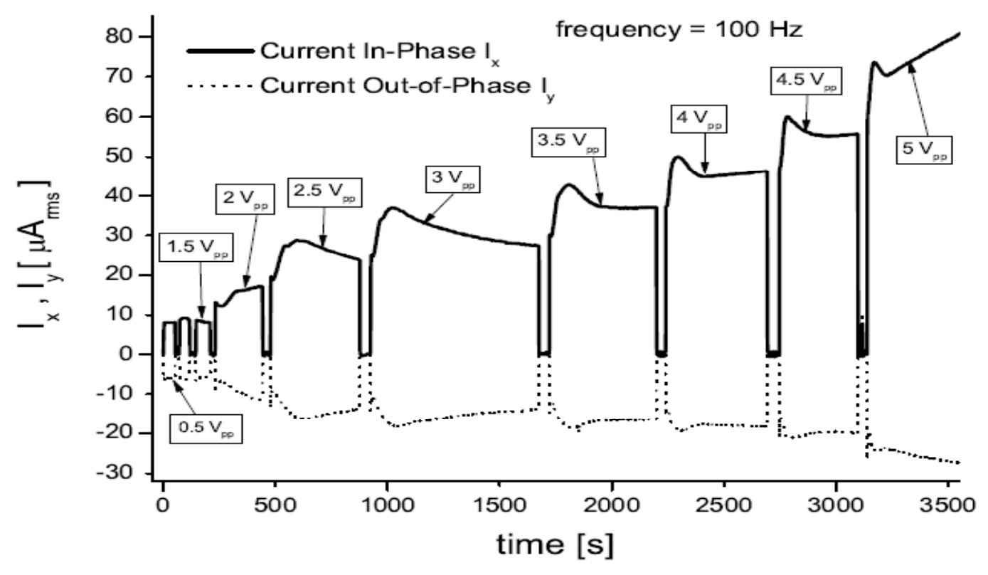
The emission of a fluorescent dye (Fluorescein) is dependent on pH. We observe a strong decrease in pH over the electrodes.



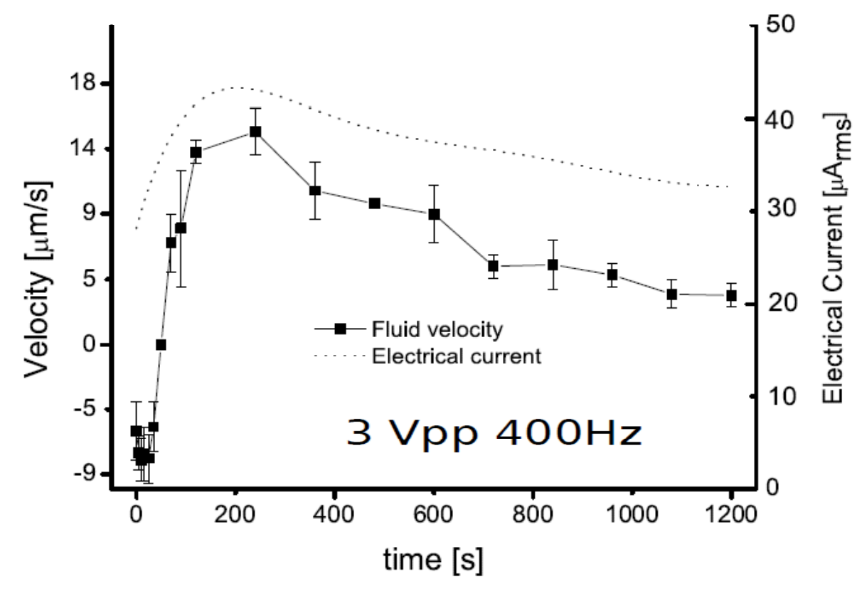
5V_{pp} 500Hz

Electrical Measurements

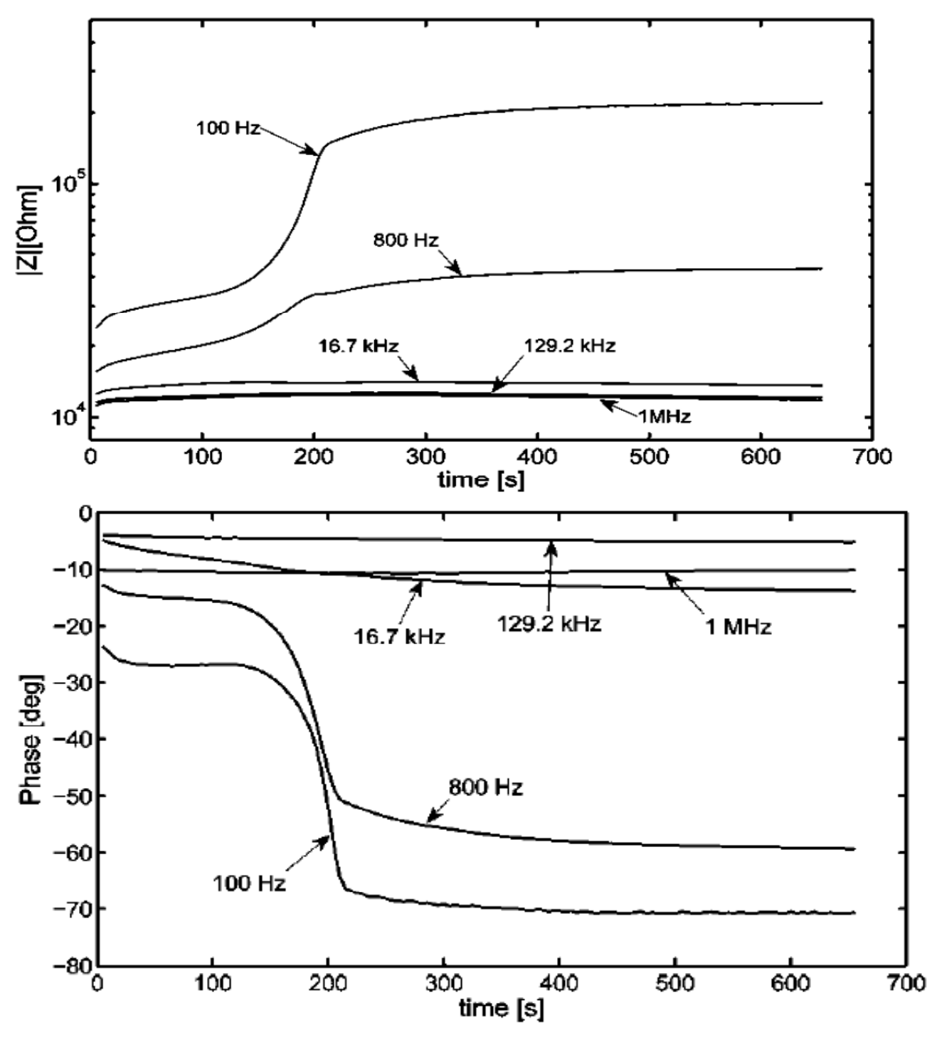
Electrical current change with time



...and changes in velocity are correlated



We measured the impedance of system after pumping for five minutes.



There is a strong decrease of impedance at low frequencies. It recovers to the initial value after approx. 200 seconds (typical diffusion time in our device).

Main Conclusions from Experiments

✓ The *fluid flow is reversed* for sufficiently high voltages

✓ We found changes in liquid properties: A *strong decrease in pH and electrical impedance*. Changes are related with the flow reversal.

✓ A strong decrease in the low frequency impedance indicates that the voltage drop is more distributed within the fluid. ⇨ *Analyze forces beyond diffuse Layer*

Forces beyond the diffuse layer

Electrical charge can be induced in electrolyte:

$$\rho + \frac{\varepsilon}{\sigma}\frac{\partial \rho}{\partial t} = \frac{\varepsilon}{\sigma}\left(\underset{(a)}{\nabla\sigma\cdot\nabla\phi} + \underset{(b)}{\sum_i e z_i D_i \nabla^2 c_i} \right)$$

Two possible origins for induced charge:
(a) *gradients of conductivity*
-supported by changes of impedance-
(b) *different mobilities* (D_i)
-supported by changes in pH-

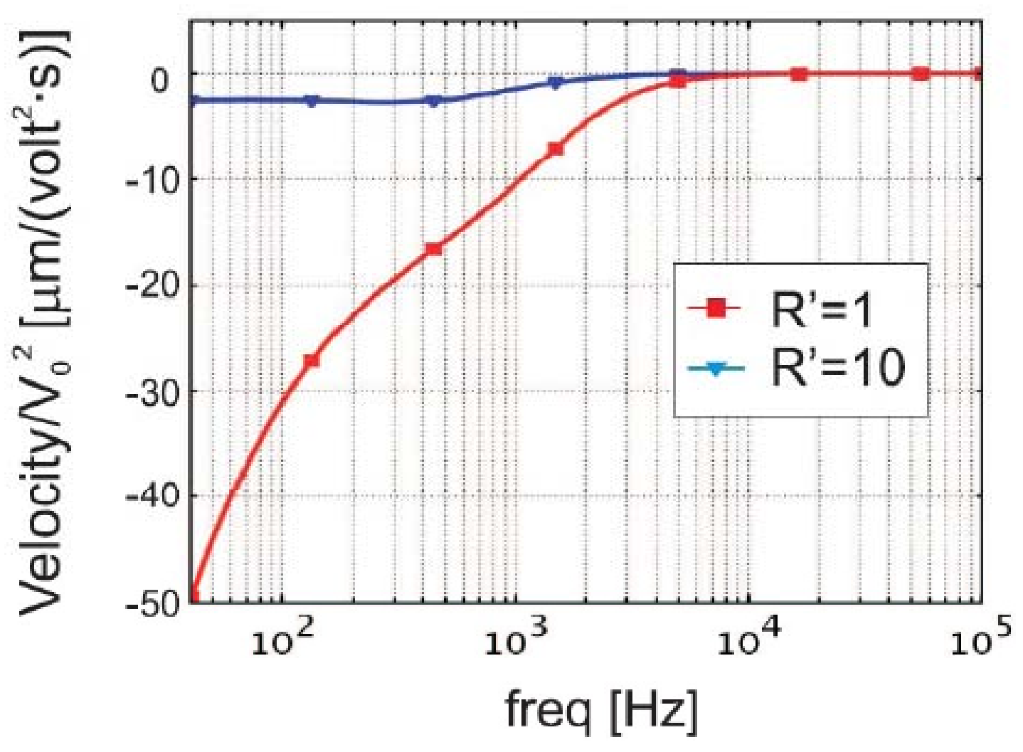
Term (b) for a binary electrolyte under quasi-electroneutrality:

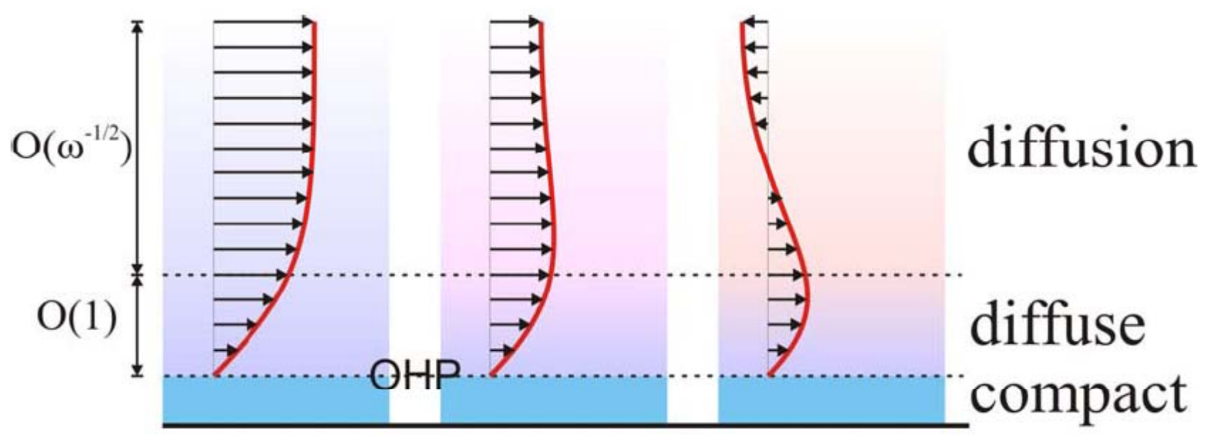
$$c_+ = c_- = c$$

$$\rho = \frac{e\varepsilon(D_+ - D_-)}{\sigma}\nabla^2 c$$

Faradaic currents can induce changes in concentration in a region of typical length $\delta=\sqrt{D/\omega}$, *the diffusion layer*.

Velocity due to charge in the diffusion layer
(small changes in concentration and assuming that the two ionic species are H^+ and Cl^-, with Faradaic currents due to reactions of H^+)





- Reverse flow is predicted by this mechanism.
In qualitative agreement with data of velocity vs frequency
- Diffusion layer stresses may overcome those in the diffuse layer and reverse the flow.

Conclusions

- Experiments on Traveling wave electroosmosis show **flow reversal and Faradaic currents** leading to changes in pH and electrical impedance.
- The inclusion of *Faradaic currents* in the electrokinetic model has great influence:

- The Electrical double layer has to be extended for accounting with the *difussion layer*.
- *Reverse flow is predicted* in the case of thick compact layer and facile reactions of the more mobile ions.

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Full Electrokinetic Problem

- Goal: Solve Poisson-Nernst-Planck and Stokes equations for a binary electrolyte subjected to a traveling-wave potential in the case of Faradaic currents and species with different mobilities.

- Poisson Equation:

$$\nabla^2\phi = -\frac{e}{\varepsilon}(c_+ - c_-)$$

- Continuity Equations for species:

$$\partial_t c_+ + \nabla\cdot\left(c_+\mathbf{v} - D_+\nabla c_+ + \mu_+ c_+\mathbf{E}\right) = 0$$
$$\partial_t c_- + \nabla\cdot\left(c_-\mathbf{v} - D_-\nabla c_- - \mu_- c_-\mathbf{E}\right) = 0$$
$$\partial_t c_0 + \nabla\cdot\left(c_0\mathbf{v} - D_0\nabla c_0\right) = 0$$

Neutral species required because electrode reactions are of the type: $X^+ + e^- \leftrightarrow X$

- Stokes equations:

$$\nabla\cdot\mathbf{v} = 0$$
$$-\nabla p + \eta\nabla^2\mathbf{v} + \rho\mathbf{E} = 0$$

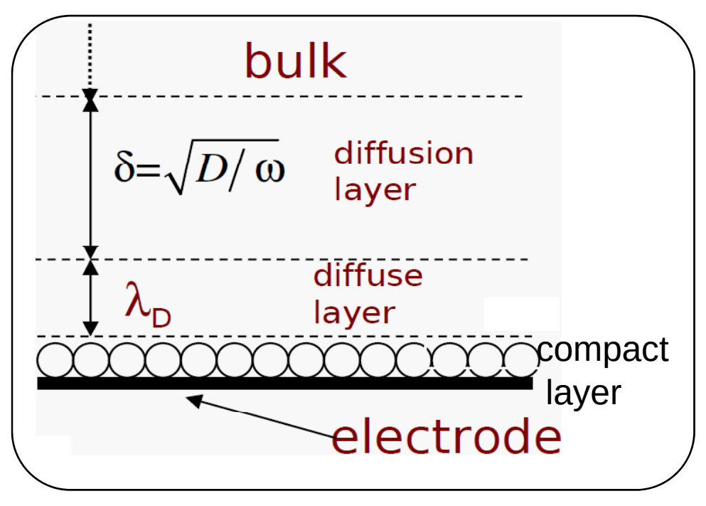
- Boundary conditions:

- Continuity of displacement vector between compact layer and electrolyte $(\varepsilon_s/\lambda_s)\Delta\phi_s = -\varepsilon\mathbf{n}\cdot\nabla\phi \text{ with } \Delta\phi_s = V_s - \phi_{y=0}$ V_s is the applied potential (for a TW, $V_s=V_0\cos(\omega t-kx)$)
- Electrodes are impermeable to negative ions, while we allow for reactions of positive ones $\mu_- c_-\mathbf{n}\cdot\nabla\phi - D_-\mathbf{n}\cdot\nabla c_- = 0,\quad -\mu_+ c_+\mathbf{n}\cdot\nabla\phi - D_+\mathbf{n}\cdot\nabla c_+ = D_0\mathbf{n}\cdot\nabla c_0 = J_F/e$

Faradaic currents are described by Butler-Volmer eq: $J_F = eK_0c_0\exp\left(\frac{\beta e\Delta\phi_s}{k_BT}\right) - eK_+c_+\exp\left(-\frac{(1-\beta)e\Delta\phi_s}{k_BT}\right)$

- Zero velocity at the Outer Helmholtz Plane (OHP) $\mathbf{v}_{y=0} = 0$

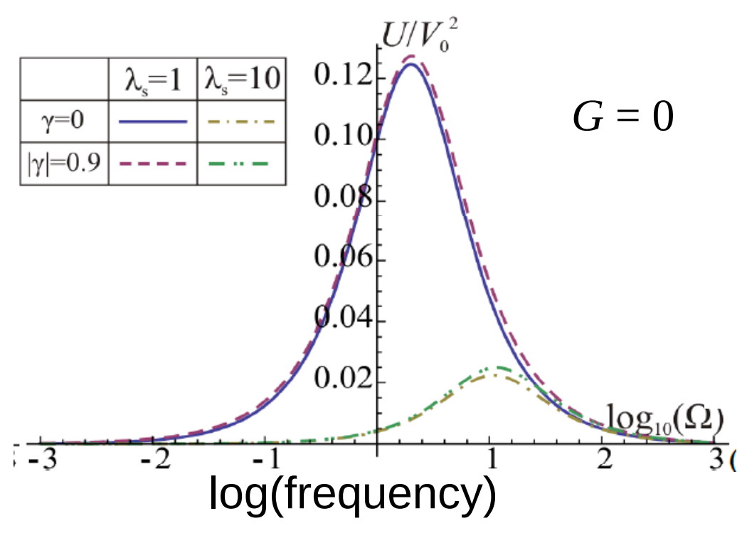
Extended Double Layer



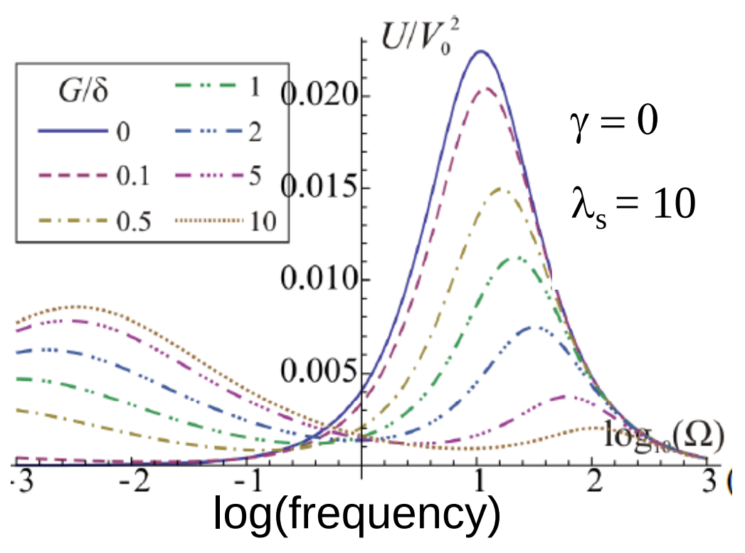
Equations are solved for small values of the applied TW potential (linearization) and using thin-layer approximation including diffusion layer, which allows us to solve:

- $\nabla^2\phi = 0$ for ϕ in the bulk, with b.c. $-\sigma\mathbf{n}\cdot\nabla\phi = Y(V_s - \phi)$ with Y a known function of parameters
- $\nabla\cdot\mathbf{v} = 0 \quad -\nabla p + \eta\nabla^2\mathbf{v} = 0$ for $\mathbf{v}$ in the bulk, with b.c. v_n=0 and v_t=v_{slip} (generalized Helmholtz-Smoluchowski formula)

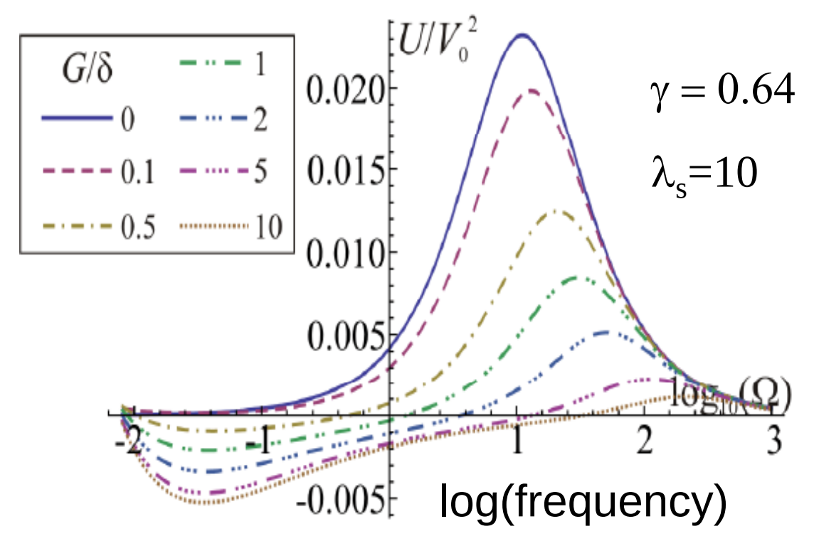
We show slip velocity against frequency for different values of:
- Reaction conductance: $G = \lambda_D K_+/2D_+$
- Ratio of diffuse layer capacitance to compact layer: $\overline{\lambda}_s = \varepsilon\lambda_s/\varepsilon_s\lambda_D$
- Asymmetry in mobilities: $\gamma = (\mu_+ - \mu_-)/(\mu_+ + \mu_-)$



No Faradaic currents:
Negligible effect of asymmetry



Faradaic currents and symmetric mobilities:
New maxima at low frequencies



Faradaic currents and asymmetry:
Reverse Flow can appear if λ_s >> 1,
(small potential drop across *Debye layer)*