

Streaming Potential near a Rotating Disk Bearing a Thin Double Layer

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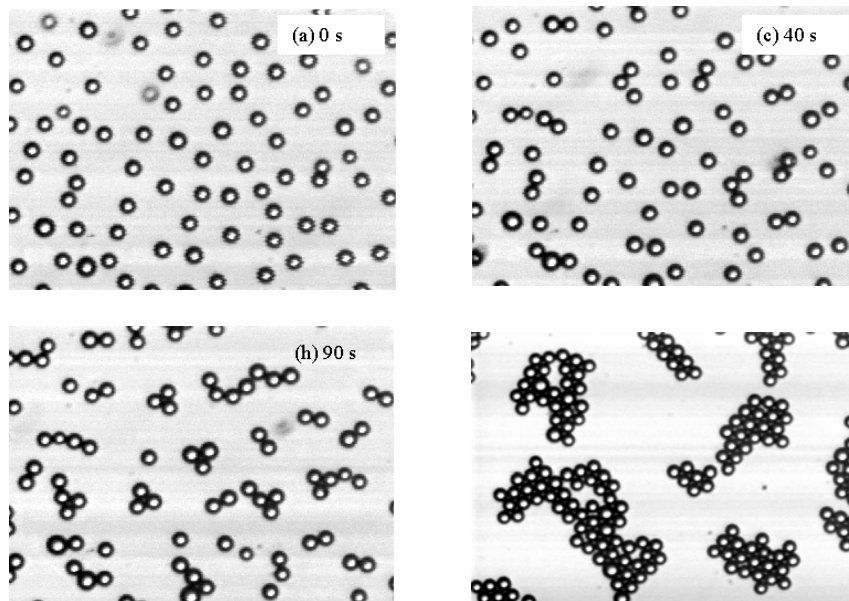
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Today I am going to describe a new method for measuring zeta potential on flat macroscopic surfaces like silicon wafers. This project grew out of an earlier one studying the formation of 2D colloidal crystals on electrode surfaces.

Aggregation on D/C Electrodes

Böhmer, *Langmuir* **12**, 5747 (1996)
Solomentsev *et al.*, *Langmuir*, **16**, 9208 (2000)
(10 μm PS in 1 mM NaHCO_3 at 60 V/m)



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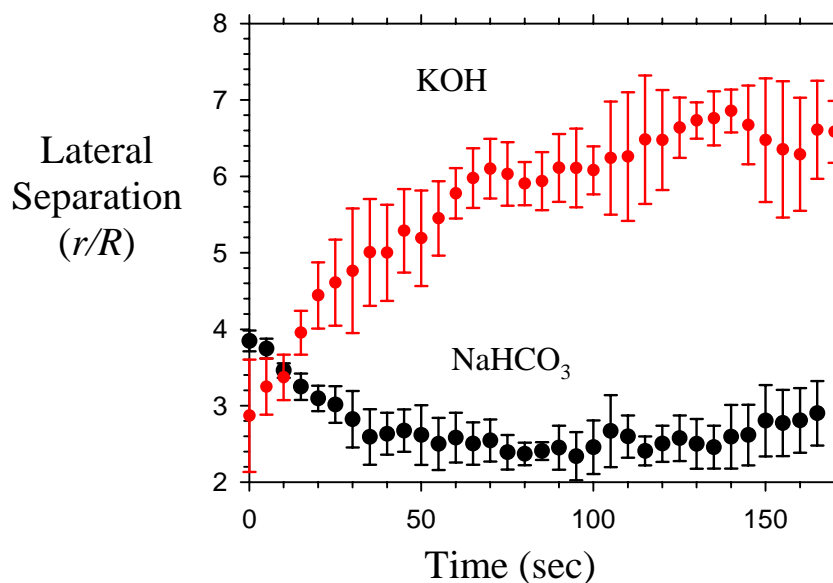
These video microscopy images show how the assembly proceeds as a function of time.

You are looking down through a microscope on the surface of a planar electrode. The particles are initially uniformly dispersed before the electric field is applied. Application of a electric field causes the particles to aggregate forming crystallites that combine to form larger crystals.

The field in these experiments is d/c. Similar results can be obtained using a/c fields although the amplitude of the field needs to be about 100x larger.

Direction Depends on Electrolyte

5.7 μm PS latex particles in 0.15 mM, 3.6 kV/m, 100 Hz



see also Kim *et al.*, *Langmuir* **18**:5387 (2002)

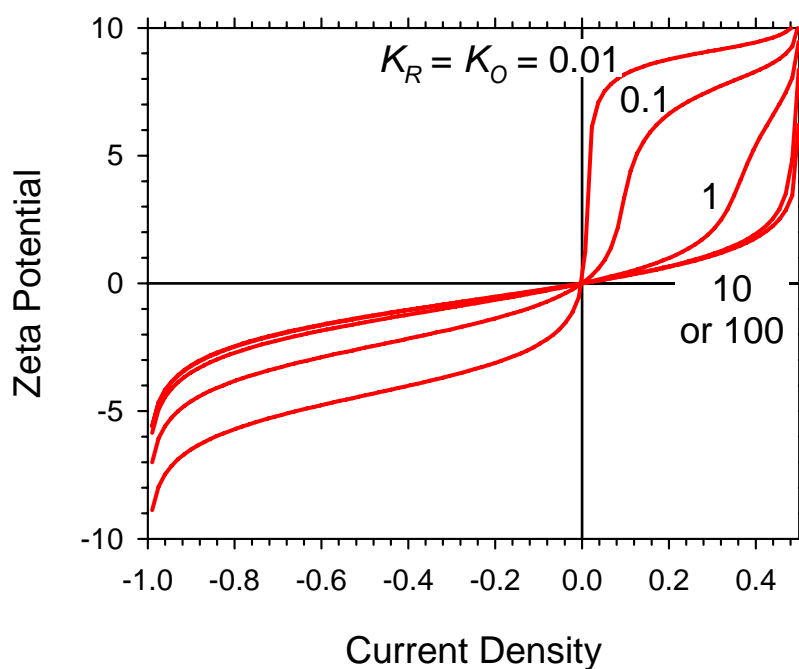
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Here are some quantitative results showing the spacing between a pair of particles on the electrode as a function of time in an *a/c* field.

Notice that two particles come together in NaHCO₃ but they move apart in KOH under otherwise identical conditions. Thus even the direction of lateral motion depends on the chemistry of the electrolyte solution. Similar results have been previously reported by Garoff and Anderson.

Yes, the pH of the electrolyte solutions is different by a couple of units but this difference does not change the sign of zeta potential on either surface.

So how does the choice of electrolyte cause opposite behavior?

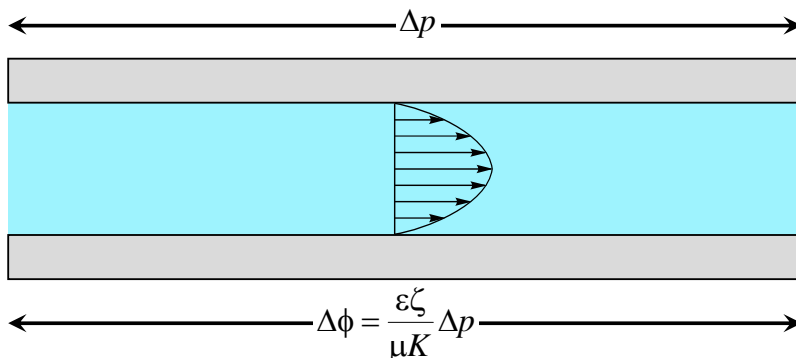
Current Perturbs Zeta PotentialPrieve, *Colloids & Surfaces A* **250**, 67 (2004)

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The answer we now believe lies with the electrode reactions. Oxidation and reduction of ions must occur on the electrode surface to exchange electronic carriers for charge in the wires for ionic carriers in the solution. Depending on which ions are present, different reactions might occur in the two different solutions.

The kinetics of the electrode reactions has an important effect on how current through the diffuse cloud changes the zeta potential. Here you are seeing how current affects zeta potential for some hypothetical reactions. Note that the rate constants (K 's) of the forward and reverse electrode reactions are important in determining how large the perturbation in zeta is.

Streaming Potential in Parallel-Plate Flowcell



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We would like to measure the effect of current on zeta potential.

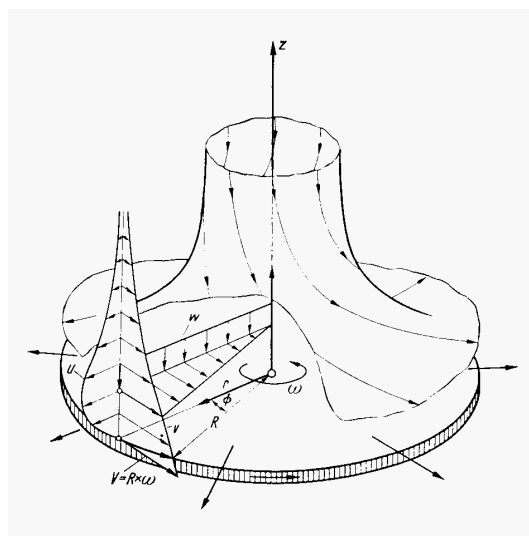
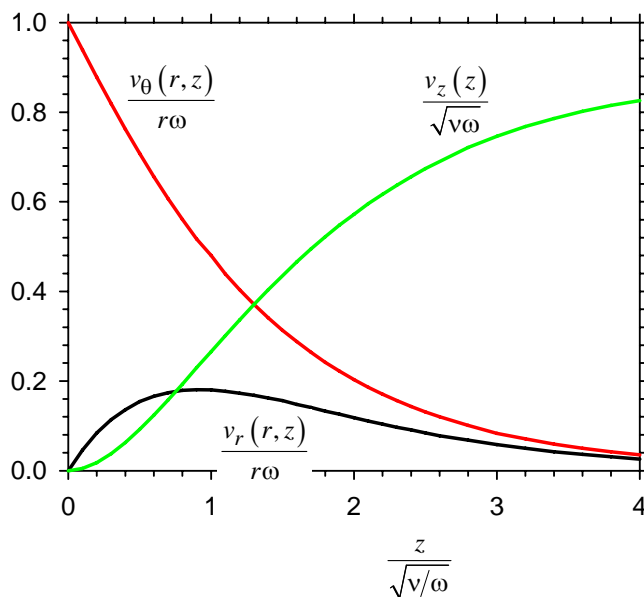
The usual device used to measure zeta potential of large flat plates is the parallel-plate flowcell shown here. Fluid is pumped by pressure along the length of the capillary causing convection of charge in the cloud next to either plate. In the absence of any return circuit, a streaming potential arises between the two ends of the capillary. That streaming potential is just enough to produce conduction of charges along the length of the capillary which just neutralizes the convection of charge, leading to zero net current.

We could easily apply a voltage difference between the two plates – this essentially is what we do in our aggregation experiments to generate a electric current normal to the electrode surface. Unfortunately the reactions at the two electrodes are opposite (oxidation at one, reduction at the other) and the zeta potential deduced from stream potential experiments would represent the average of the two surfaces.

If the perturbations were equal in magnitude but opposite in sign on the two electrodes, no perturbation in streaming potential would be measured. It is not apparent how to measure separately the perturbation in zeta on either electrode.

Hydrodynamics of Rotating Disk

Th. von Kármán (1921) and W.G. Cochran (1934)



$$2R = 25 \text{ mm}$$

$$\sqrt{\nu/\omega} = 2 \text{ mm for } \omega = 1000 \text{ rpm}$$

$$\kappa^{-1} = 30 \text{ nm for } 0.1 \text{ mM}$$

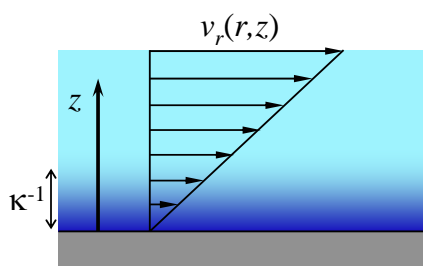
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In the rotating disk experiment, convection is driven by the rotation of the disk rather than an applied pressure drop. The circular motion of the disk causes centripetal force on the fluid driving outward radial flow. Continuity then requires fluid to be drawn axially toward the disk, resulting in all components of fluid velocity being nonzero.

This is one of only two or three flow problems where both inertia and viscous forces are important but an exact solution of the Navier-Stokes equations is known.

The momentum boundary thickness depends on the rotation speed of the disk and the kinematic viscosity of the fluid. For a disk rotating at 1000 rpm in water, this thickness is about 2mm which is 5 orders of magnitude larger than the Debye length. Thus the counterion cloud can be treated as being very thin.

Radial Convection of Electric Current

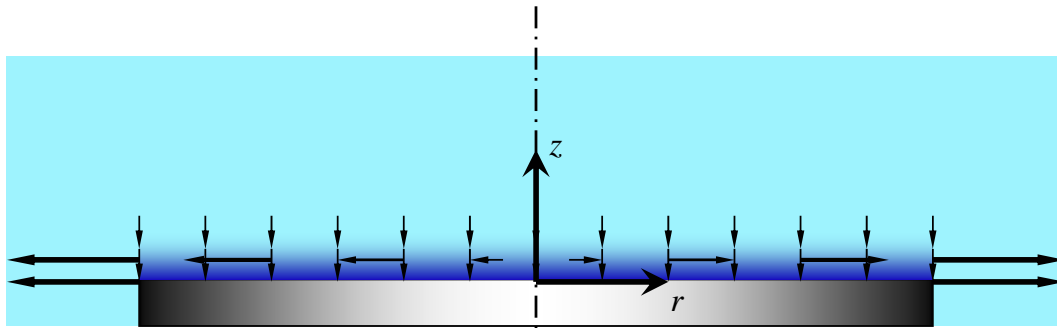


$$I_r = \int_0^{\kappa^{-1}} i_r dz = \int_0^{\kappa^{-1}} \rho v_r dz = -\epsilon \Gamma \int_0^{\infty} z \frac{d^2 \psi}{dz^2} dz = -\epsilon \Gamma \zeta$$

$\rho = -\epsilon \frac{d^2 \psi}{dz^2}$	$v_r = \Gamma z$
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While there is convection of charge in the theta direction, this does not contribute to the streaming potential. Instead, it is the radial flow which is important. The radial convective current can be calculated by integrating the local current density across the counterion cloud. The local current density is the product of the local charge density and the local radial fluid velocity. Using Poisson's equation for the charge density and linear-shear for the flow we obtain an integral which can be integrated by parts twice. This yields a total radial convection of charge which is proportional to the potential drop across the cloud (which is the zeta potential) and the shear rate.

Conservation of Charge



$$I_r = -\varepsilon\Gamma\zeta = -\varepsilon\zeta r\omega^{3/2}v^{-1/2}F'(0) = Ar$$

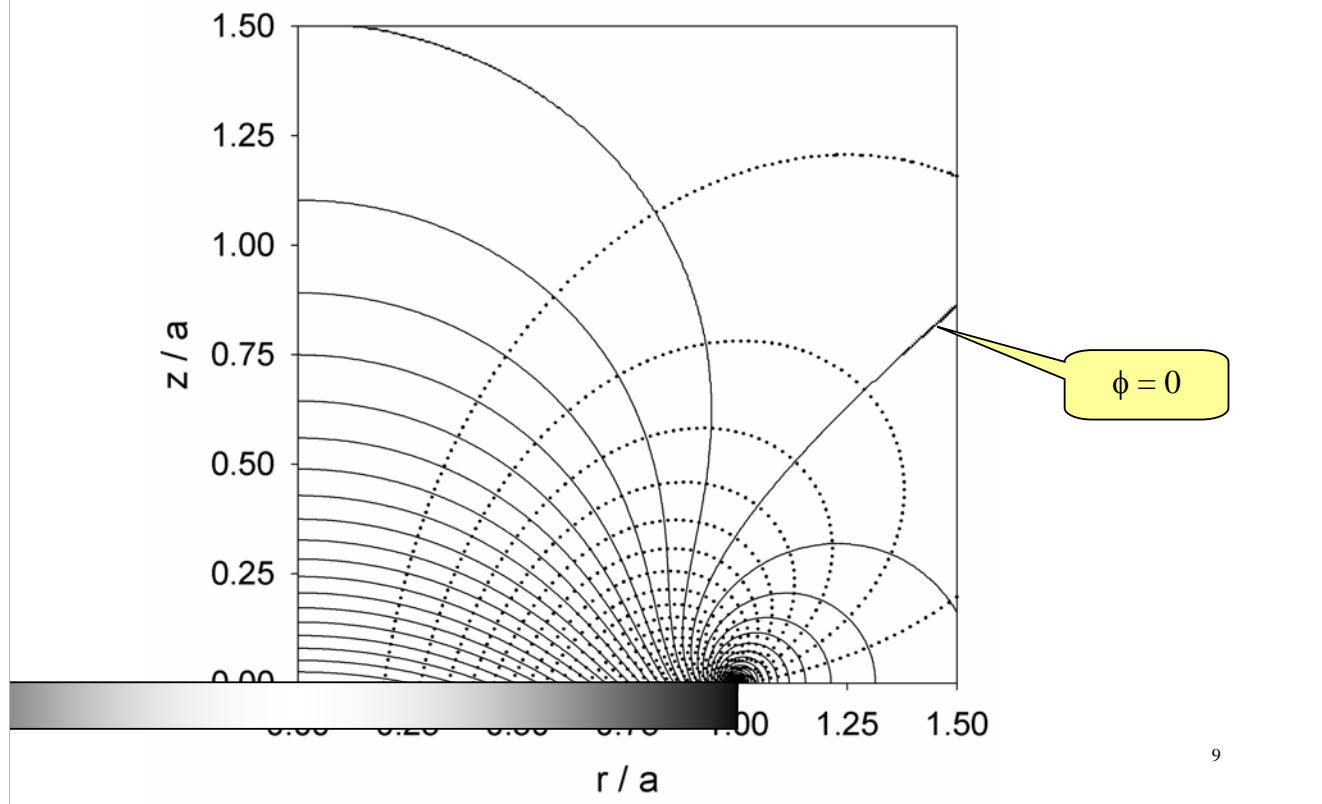
$$\Gamma = \frac{\partial v_r}{\partial z} = \frac{\partial}{\partial z} \left[r\omega F \left(\frac{z}{\sqrt{v/\omega}} \right) \right] = r\omega \sqrt{\frac{\omega}{v}} F'(0)$$

$$\int_0^{\kappa^{-1}} \nabla \cdot \mathbf{i} dz = 0 \quad \Rightarrow \quad i_z|_{\kappa^{-1}} = -\frac{1}{r} \frac{\partial}{\partial r} (rI_r) = -2A$$

Since the radial fluid velocity is proportional to r , so the radial convection of charge is also proportional to r . Thus the radial current is not uniform. Conservation of charge requires a uniform axial current to supply the uniformly increasing radial current.

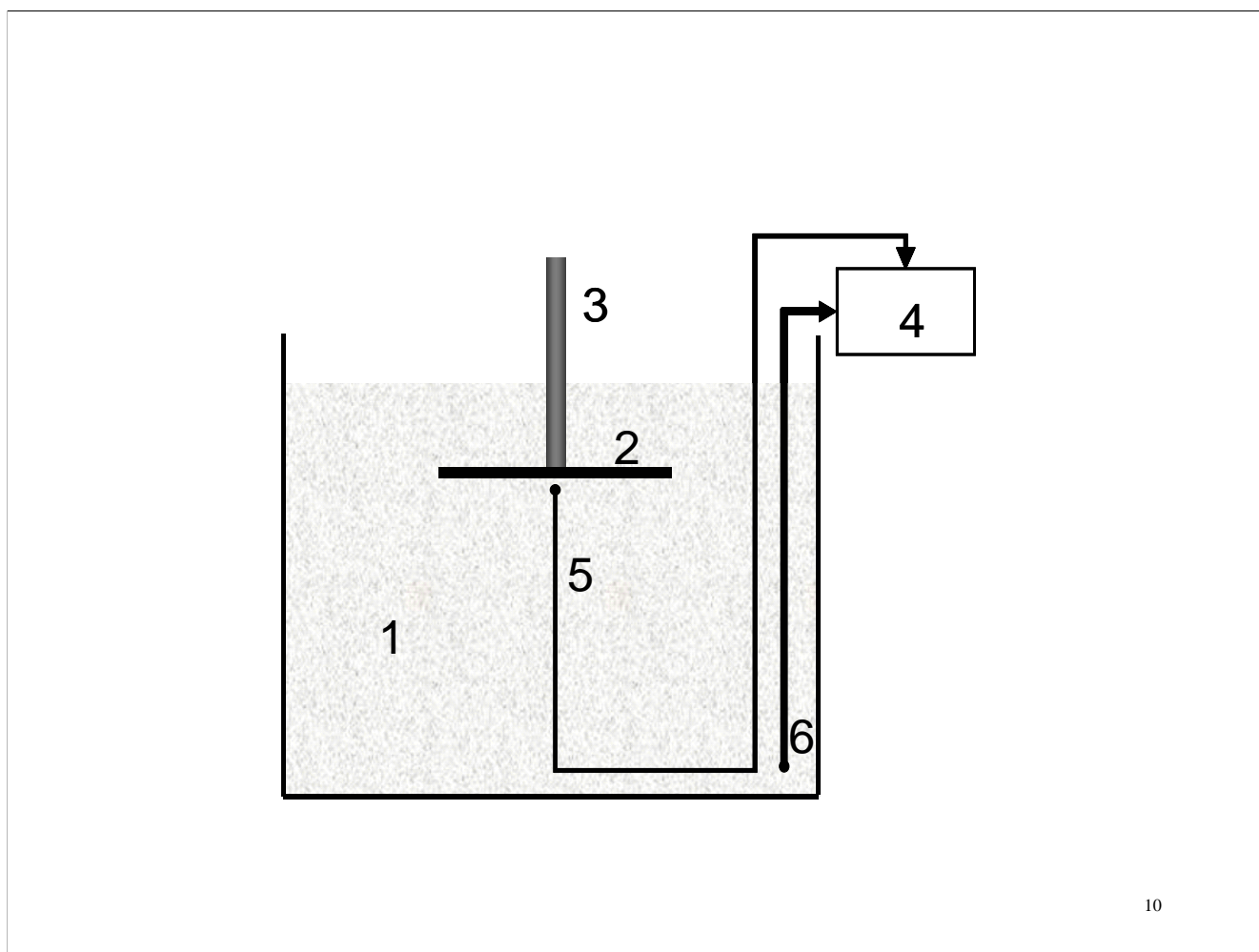
So the boundary conditions for the outer problem are uniform axial current density into the surface of the disk and an equal current radially outward at the edge of the disk. Outside the diffuse charge cloud, these currents are by conduction driven by an electric field arising from the streaming potential.

Solution for ϕ and Field Lines



The solution to this electrostatics problem is straightforward and is summarized by this slide. The solid curves are isopotential contours while the dotted lines are field lines represent the trajectories taken by charge. Recall that the current was radially outward near the outer edge of the disk. These trajectories curve upward and turn back into the disk axially.

The reference state for potential is the solution far from the disk. As it turns out, one of these isopotential contours intersecting with the surface of the disk corresponds to this reference state ($\phi = 0$). This contour intersects the disk at about 85% of its radius.

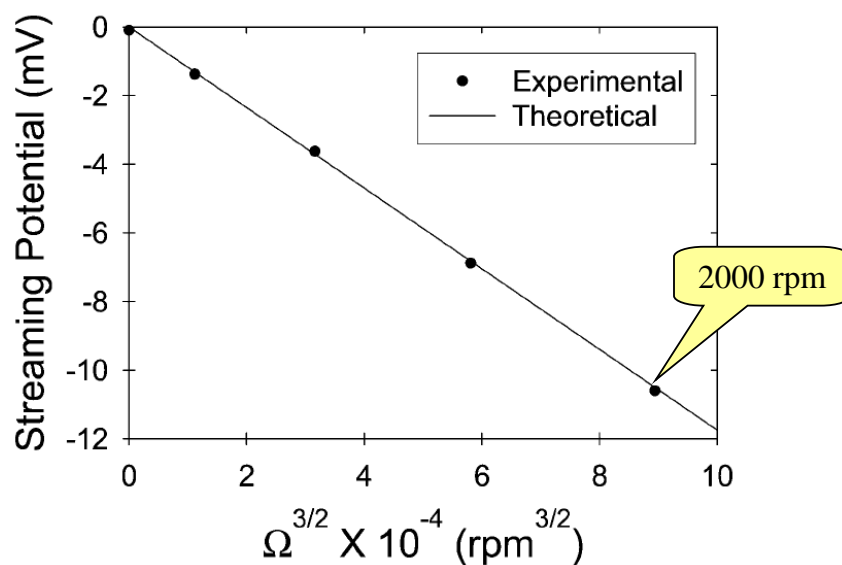


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The experiment is quite simple. The disk (2) is mounted on the end of a spindle (3) which is immersed in an electrolyte solution (1) contained in a beaker. Silver wires tipped with AgCl are used as electrodes (5 and 6). The wires are insulated except for their tips. One electrode (5) is placed on the axis of rotation near the surface of the disk and serves as the working electrode. The other electrode (6) is located far from the disk and serves the reference. The potential measured between them is the streaming potential.

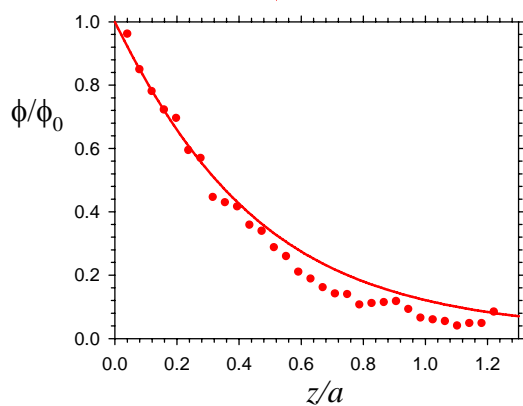
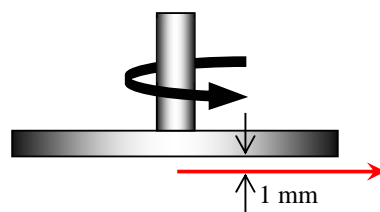
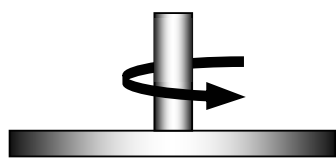
Check Dependence on Rotation Speed

Silicon Wafer in KCl with Conductivity $1.45 \mu\text{S/cm}$
[Hoggard *et al.*, *Langmuir* **21**, 7433 (2005)]

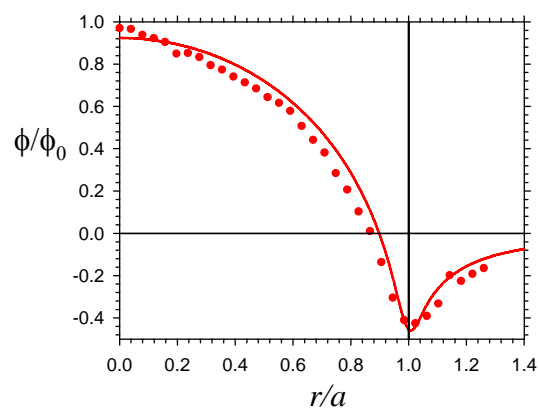


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Now some experimental results. The theory predicts that the streaming potential should everywhere be proportional to the $3/2$ power of rotation speed. This slide shows that the measured streaming potentials are indeed proportional to the $3/2$ power as expected.

Check on Shape of Profiles5cm Silicon Wafer ($\zeta = 74$ mV), KCl solution ($1.8 \mu\text{S}/\text{cm}$), 1500 rpm

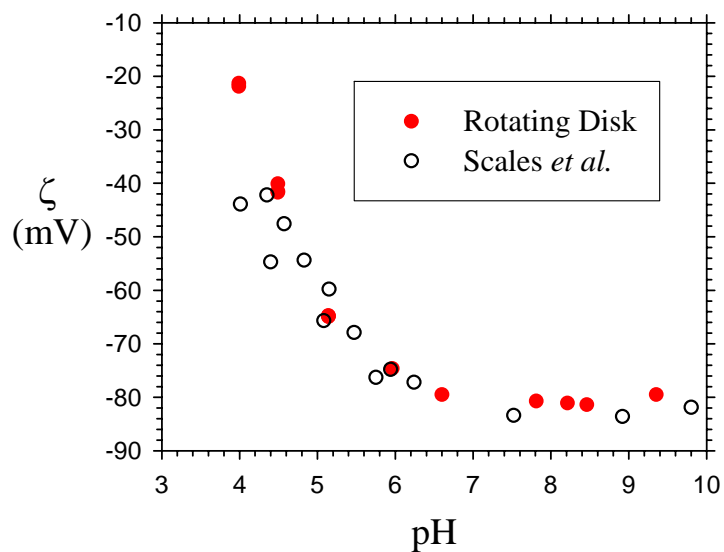
$$\phi_0 = 7.6 \text{ mV}$$



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Some Typical Results

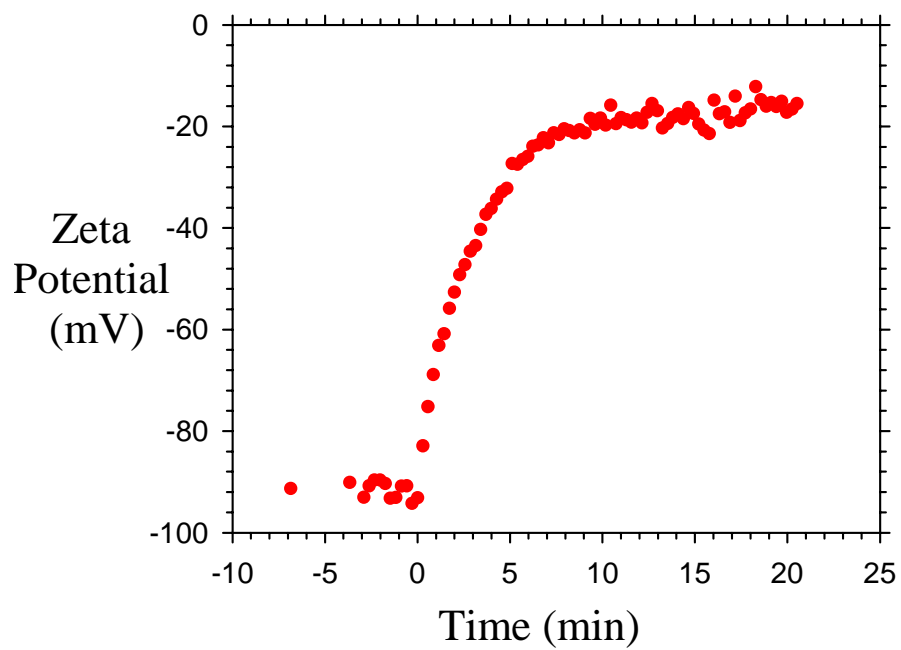
Mica Disks in 1 mM KCl + KOH or HCl



Scales, P.J. *et al.*, *Langmuir* **6**, 582 (1990)

Dynamics of Adsorption

0.2 mg/L Polymerized Micelles Adsorbing onto Mica in 0.65 mM KCl



Advantages of Rotating Disk vs. Parallel Plate Flowcell

- Don't need 2 matching plates
- Leaks are not a problem
- Good mixing – rapid titration
- Can isolate effect of current on one electrode