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Electrokinetics and Electrohydrodynamics of Microsystems

Induced-Charge Electrokinetic Phenomena

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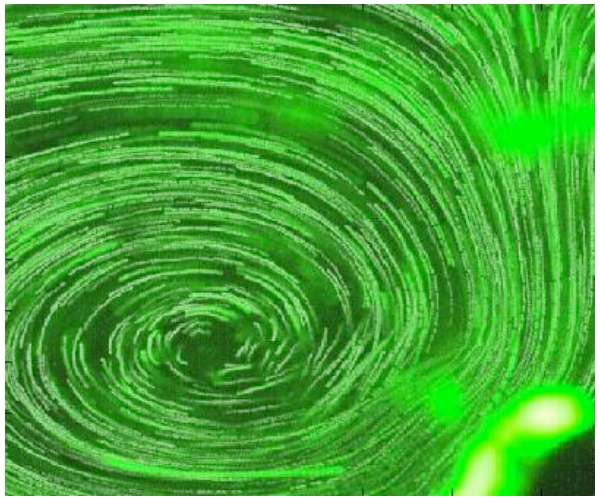
Lectures

1. Introduction
2. Low-voltage theory
3. Particle motion
4. Fluid motion
5. Large-voltage theory

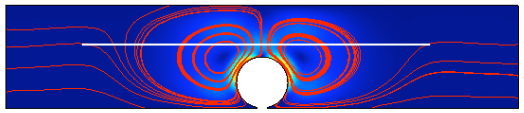


Experimental Puzzles

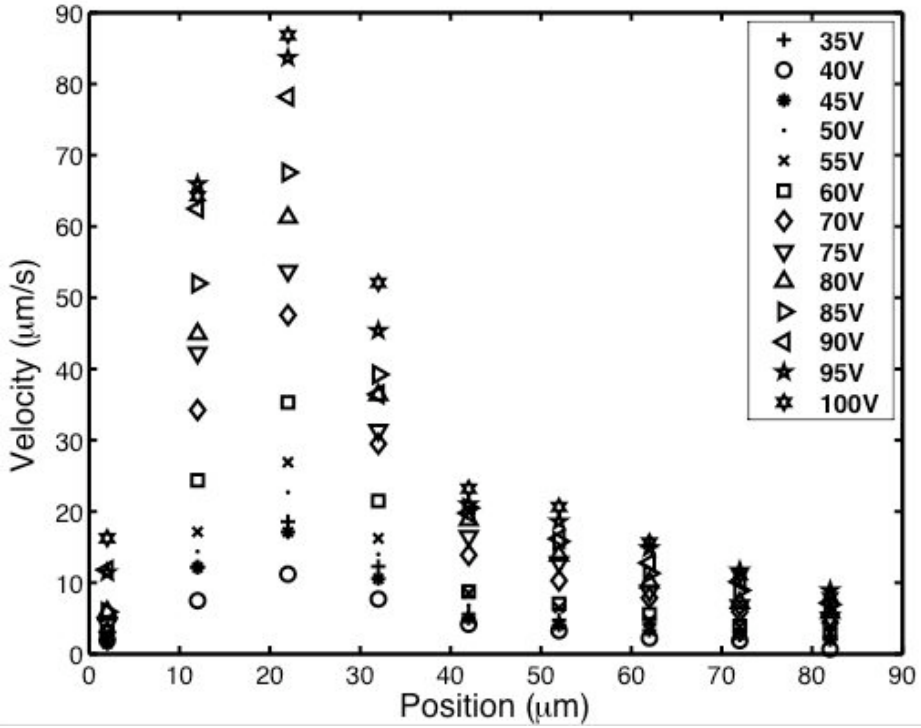
Low voltage theory vs. experiment

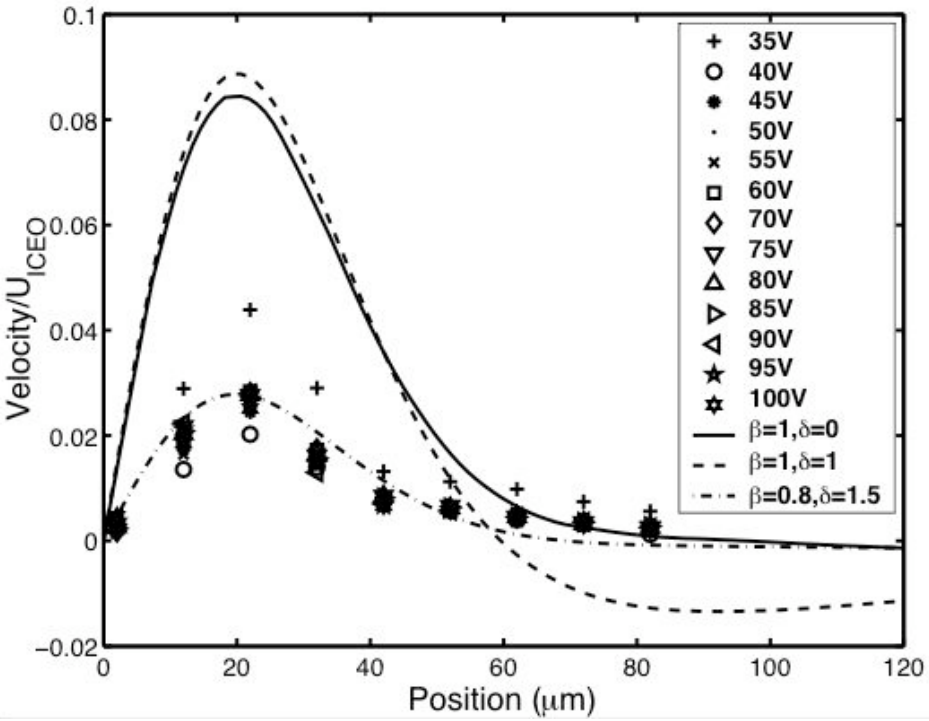
Levitan et al (2005)

Horiz. velocity from a slice 10 μm above the wire



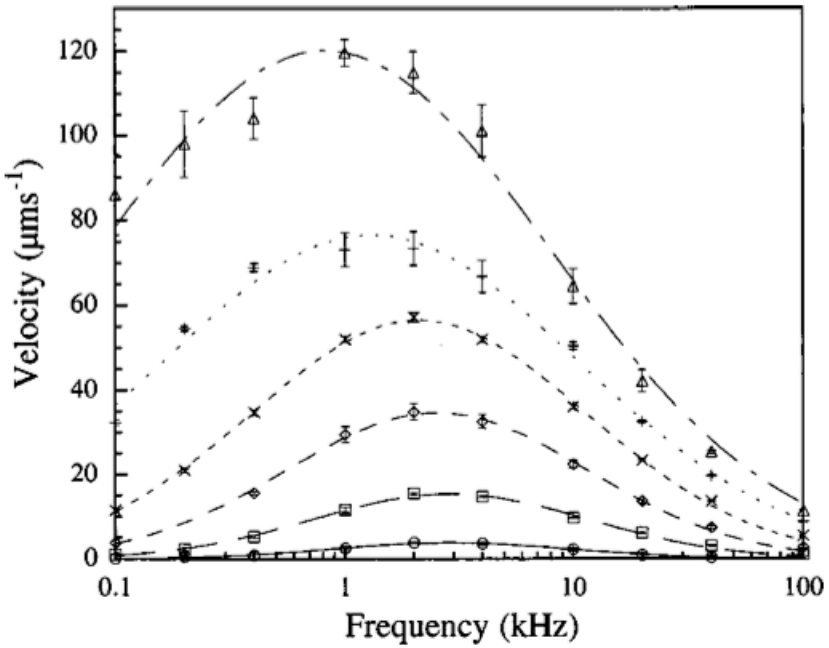
Data collapse when scaled to characteristic ICEO velocity

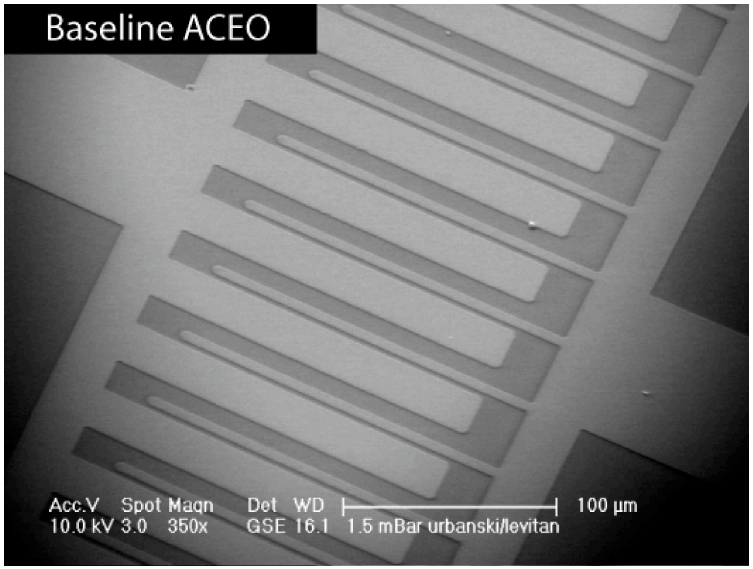




- Scaling and flow profile consistent with theory
- Velocity is 3 times smaller than expected (no fitting)
- *BUT this is only for dilute 0.1 mM KCl…flow vanishes above 10mM!*

Low-voltage ACEO data





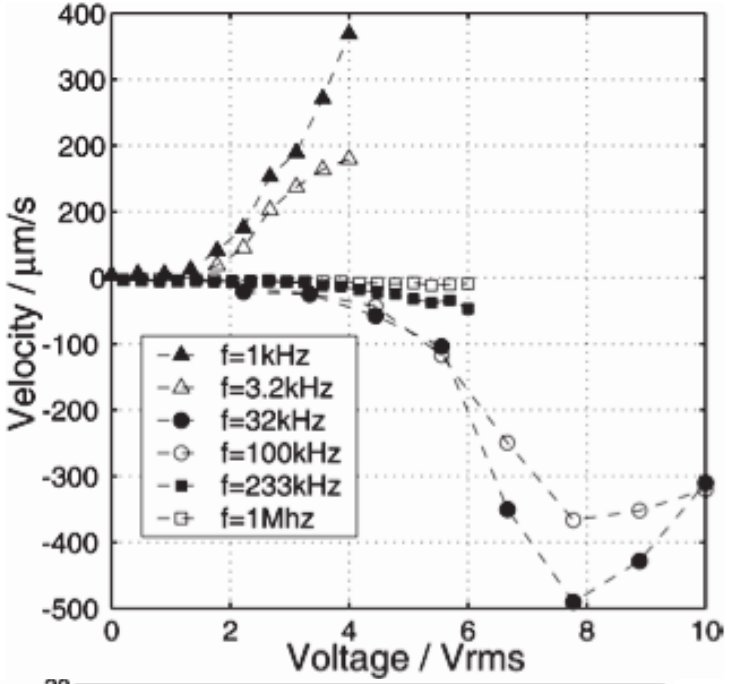
Brown et al (2001), water
- straight channel
- planar electrode array
- similar to theory (0.2-1.2 Vrms)

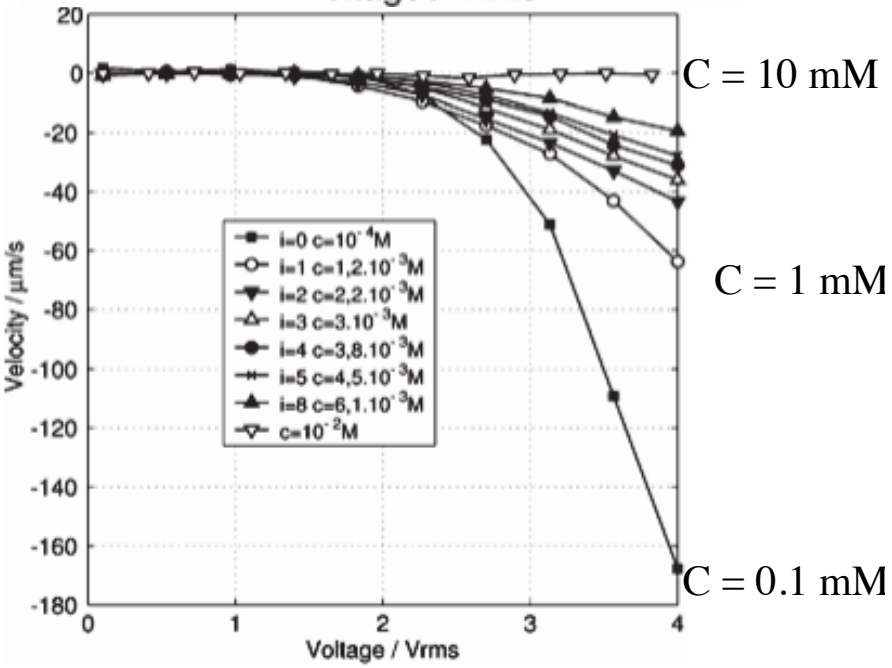
Reproduced in < 1 mM KCl
Studer 2004
Urbanski et al 2006

High-voltage data

V. Studer et al. Analyst (2004)

- Dilute KCl
- Planar electrodes, unequal sizes & gaps
- Flow reverses at high frequency
- Flow effectively vanishes > 10 mM.

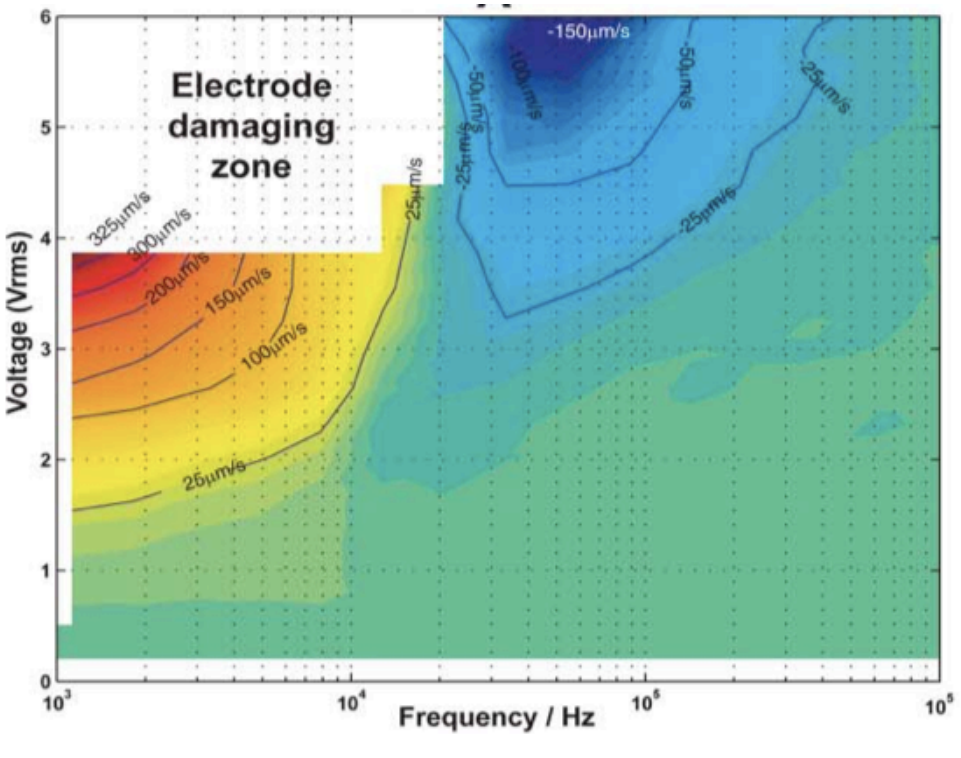




C = 10 mM

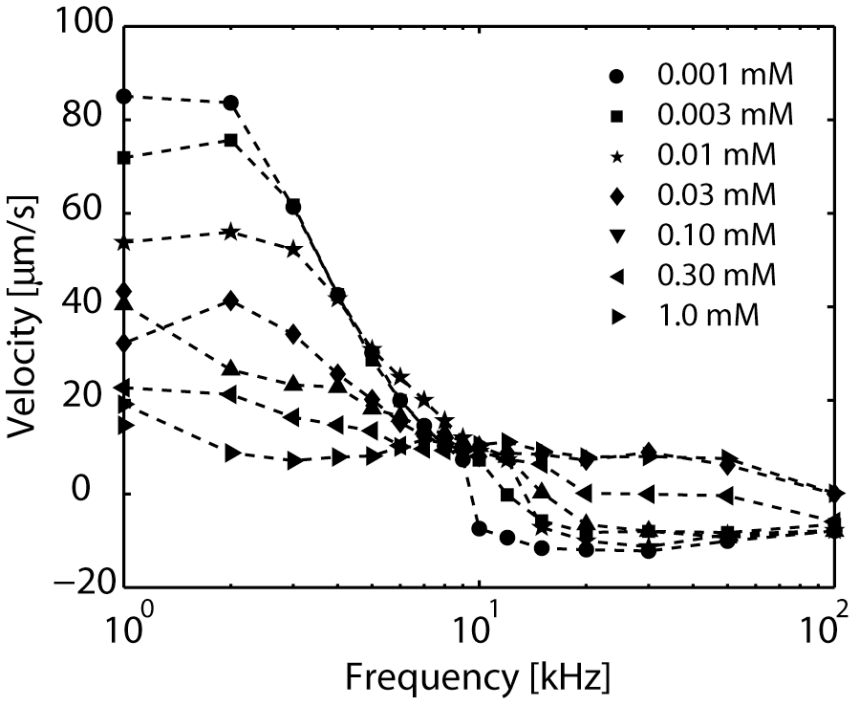
C = 1 mM

C = 0.1 mM



More puzzling high-voltage ACEO data

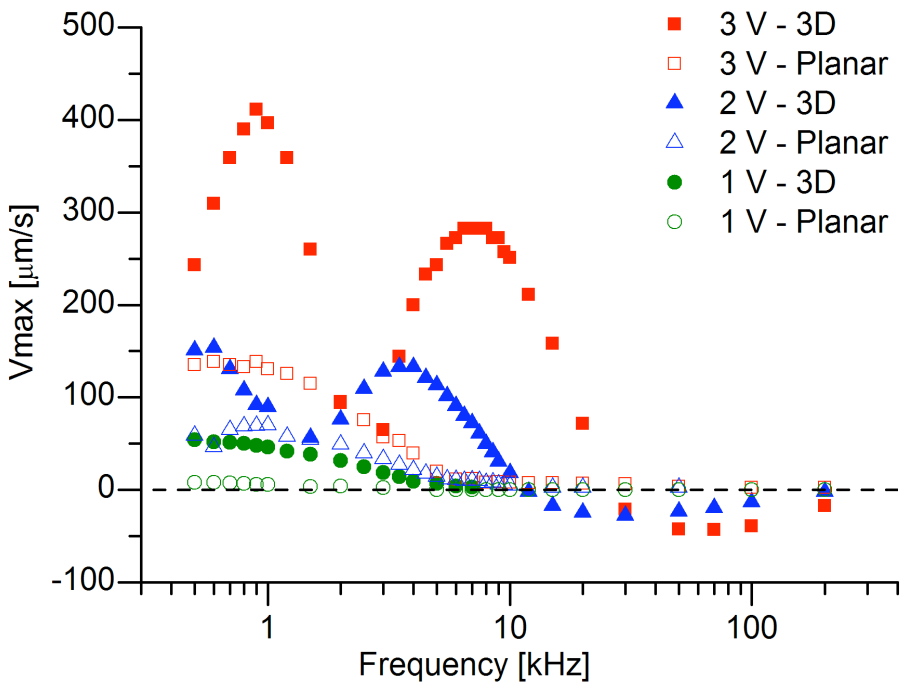
Bazant et al, MicroTAS (2007)



KCl, 3 Vpp, planar pump

Reversal at high frequency?
Concentration decay?

Urbanski et al, Appl Phys Lett (2006)



De-ionized water (pH = 6)

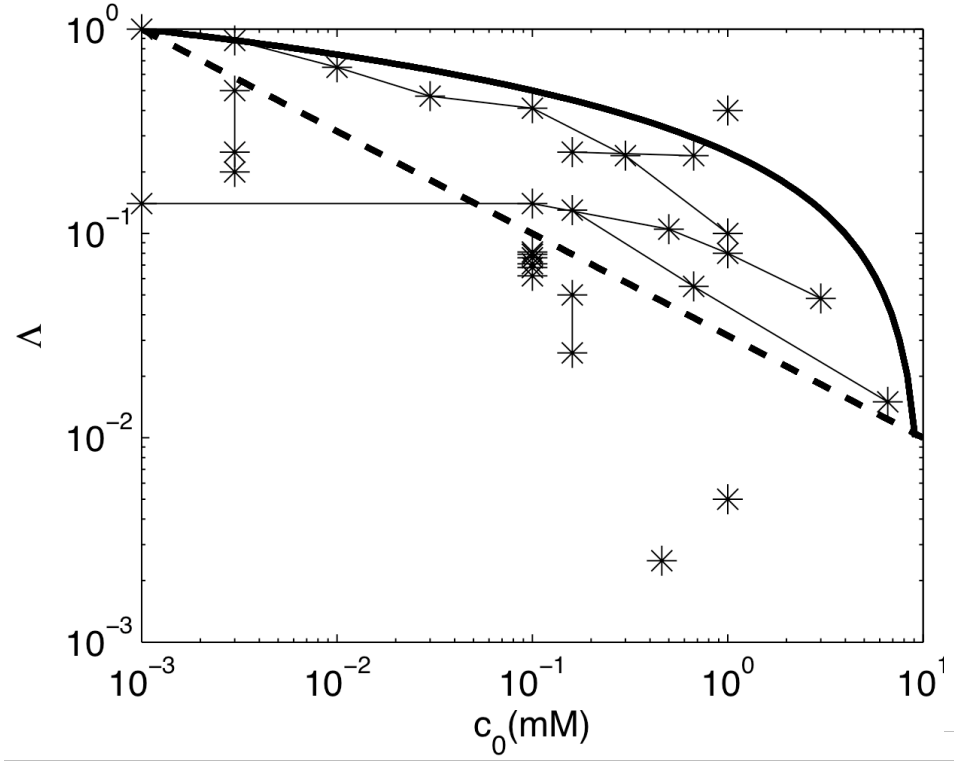
Double peaks?

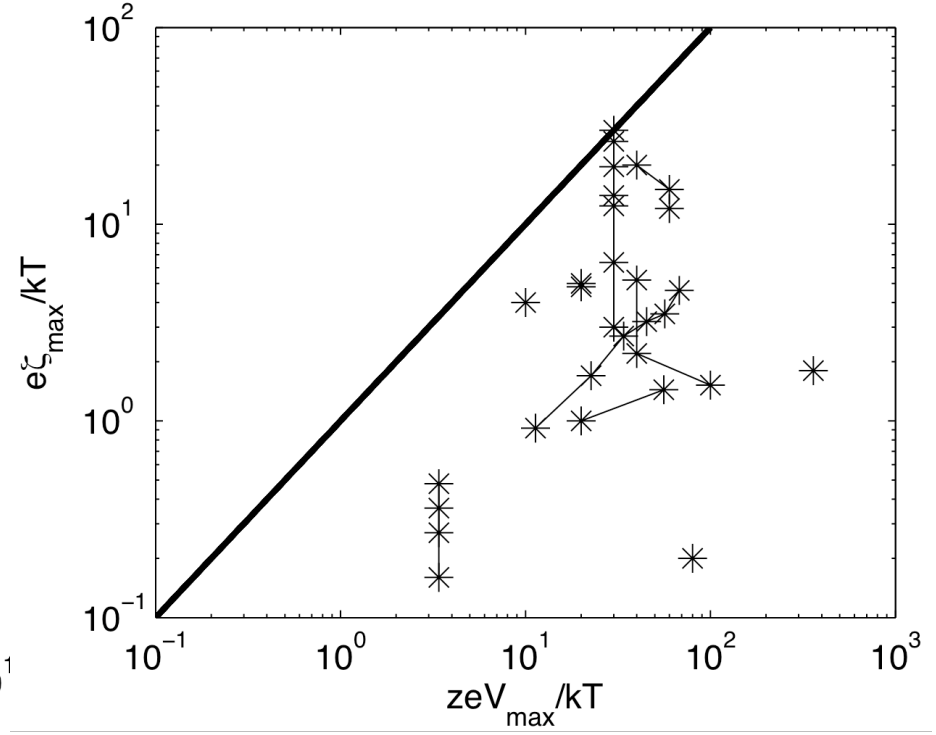
The "correction factor" $u_s = \Lambda \frac{\varepsilon \zeta E}{\eta}$

Reference	Type of Flow	Solution	c_0	$V_{max}^{induced}$	Λ	ζ_{max}	$e\zeta_{max}/kT$
Green et al. 2000 [28]	ACEO electrode pair	KCl	0.16mM	1.0 V	0.13	0.13 V	5.2
			0.67mM	1.0 V	0.055	0.055 V	2.2
			6.6mM	2.5 V	0.015	0.038 V	1.52
Green et al. 2002 [30]	ACEO electrode pair	KCl	0.16mM	0.5 V	0.25‡	0.125 V	5
			0.67mM	0.5 V	0.24‡	0.12 V	4.8
Ramos et al. 2005 [45]	TWEO electrode array	KCl	0.16mM	0.5 V	0.05	0.025V	1
				1.4V	0.026	0.036 V	1.44
Bown et al. 2006 [80]	Disk electrode ACEO	KCl	0.43mM	2.0 V	0.0025	0.005 V	0.2
Urbanski et al. 2007 [43]	3D ACEO array	KCl	3μM	1.5 V	0.2*	0.3 V	12
Bazant et al. 2007 [38]	planar ACEO array	KCl	0.001mM	0.75 V	1*	0.75 V	30
			0.003mM		0.88*	0.66 V	26.4
			0.01mM		0.65*	0.49 V	19.6
			0.03mM		0.47*	0.35 V	14
			0.1mM		0.41*	0.31 V	12.4
			0.3mM		0.24*	0.18 V	6.4
			1mM		0.10*	0.075 V	3
Storey et al. 2008 [62]	planar ACEO array	KCl	0.03mM	0.75 V	0.667	0.5 V	20
Levitan et al. 2005 [17]	metal cylinder ICEO	KCl	1mM	0.25 V	0.4‡	0.1 V	4
Soni et al. 2007 [88]	fixed-potential ICEO	KCl	1mM	9.0 V	0.005	0.045	1.8
Brown et al. 2001 [31]	ACEO array	$NaNO_3$	0.1mM	1.7V	0.068*	0.115V	4.6
				1.41V	0.062*	0.087 V	3.5
				1.13V	0.071*	0.08 V	3.2
				0.85V	0.079*	0.067 V	2.7
				0.57V	0.076*	0.043 V	1.7
				0.28V	0.081*	0.023 V	0.92
Urbanski et al. 2006 [37]	ACEO array	water	$\approx \mu$M	1.5 V	0.25*	0.375 V	15
				1.0 V	0.5*	0.5 V	20
Gangwal et al. 2008 [22]	Janus particle ICEP	water	$\approx \mu$M	0.085 V	0.14†	0.012 V	0.48
Kilic & Bazant 2008 [51]		NaCl	0.1mM		0.14†	0.012 V	0.48
			0.5mM		0.105†	0.009 V	0.36
			1mM		0.08†	0.007 V	0.27
			3mM		0.048†	0.004 V	0.16

Trends in the correction factor

Bazant, Kilic, Storey & Ajdari, arxiv preprint, submitted to ACIS (2009)



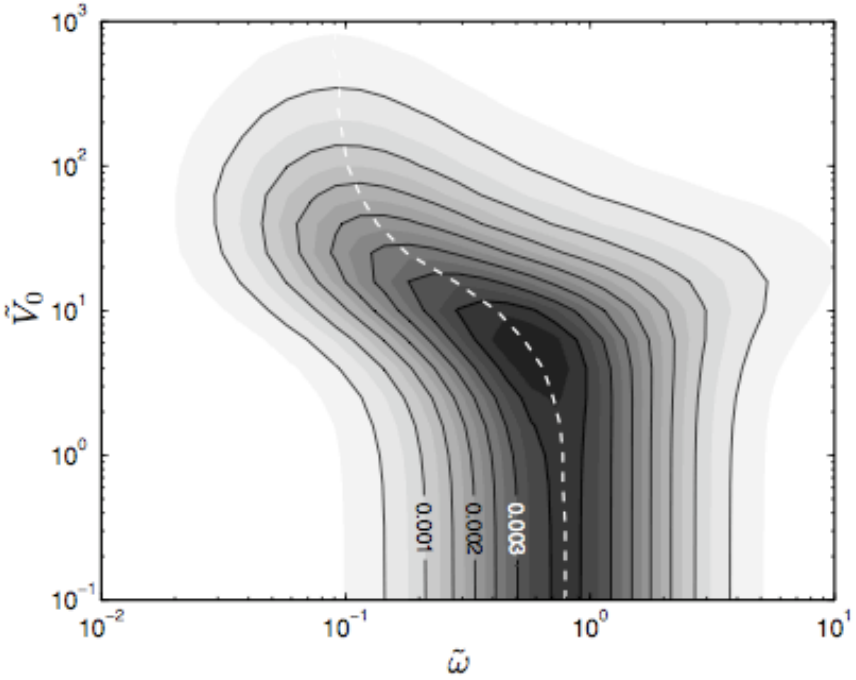


-Strong decay with concentration above mM salt

- Zeta potential saturates < 10 kT/e = .25 V

Weakly nonlinear AC electro-osmosis

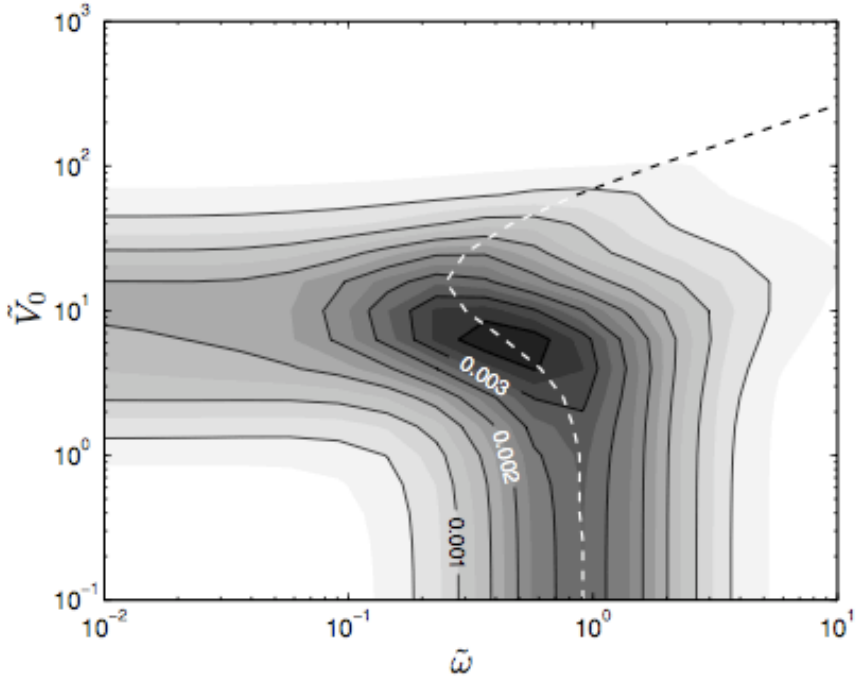
Olesen, Bruus, Ajdari, Phys. Rev. E (2006).



Nonlinear DL capacitance shifts flow to low frequency

$$C_D = \frac{\varepsilon}{\lambda}\cosh\left(\frac{ze\Psi_D}{2kT}\right)$$

Simulations of U vs log(V) and log(freq):

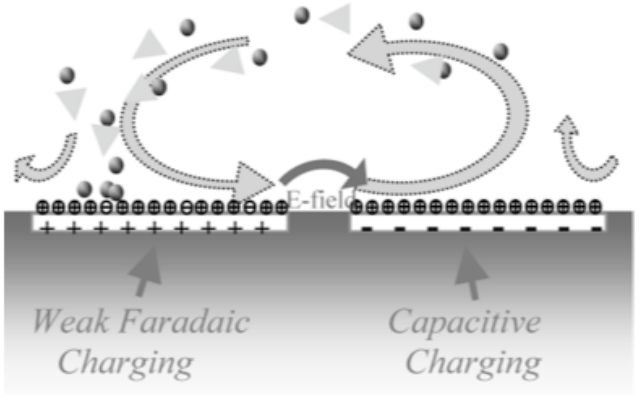


Faradaic reactions "short circuit" the flow

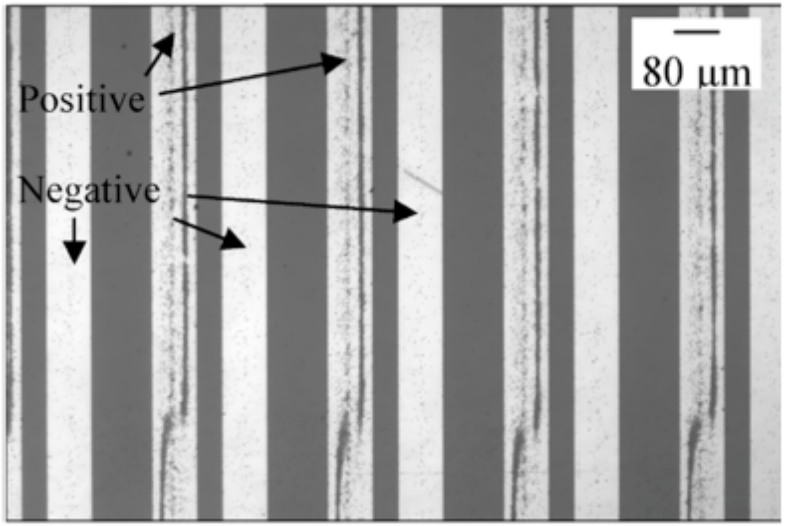
Classical models fail…

Faradaic reactions

- Ajdari (2000) predicted weak low-frequency flow reversal in planar ACEO pumps due to Faradaic reactions
- Observed by Gregersen et al (2007)
- Lastochkin et al (2004) attributed high frequency ACEO reversal to reactions, but gave no theory
- Olesen, Bruus, Ajdari (2006) could not predict realistic ACEO flows with linearized Butler-Volmer model of reactions
- Wu et al (2005) used DC bias + AC to reverse ACEO flow
- Still no mathematical theory



Wu (2006)



ACEO trapping *e Coli* bacteria with DC bias

Strongly nonlinear dynamics

Bazant, Thornton, Ajdari PRE (2004), Chu & Bazant, PRE (2006);
Laurits Olesen, PhD Thesis, Technical University of Denmark (2006)

New “physical” effects

- Neutral salt adsorption by highly charged double layers
- Bulk diffusion, concentration polarization
- Surface conduction “short circuits” double-layer charging
- Diffusio-osmosis & bulk electroconvection oppose ACEO
- Space-charge and “2nd kind” electro-osmotic flow

New “chemical” effects

- Specific adsorption of ions on electrodes
- Faradaic reactions (electrolysis of water + ???)
- voltage-dependent water equilibrium (pH, pK…)

A Crazy Idea (Blasphemy!)

Maybe it is time to question the validity of the Standard Model, rather than just to solve it more accurately.

Indeed, the classical electrokinetic equations assume many things:

- point charges in a dielectric continuum
- mean-field approximation
- constant material properties (permittivity, viscosity,…)

… which are only valid for a dilute solution at low voltage.

Beyond the Standard Model

History of the "magnum opus"

- 2005 Ajdari at MIT
- 2006 presented at ELKIN, posted arxiv.org
- 2007 rejected by Phys Rev Lett
- 2009: grew to 70 pages, 300 refs, 22 figs…
- Likely to appear in ACIS 2009, draft at arxiv.org
- 2007 PRL published in New J Phys 2009

Towards an understanding of induced-charge electrokinetics at large applied voltages in concentrated solutions

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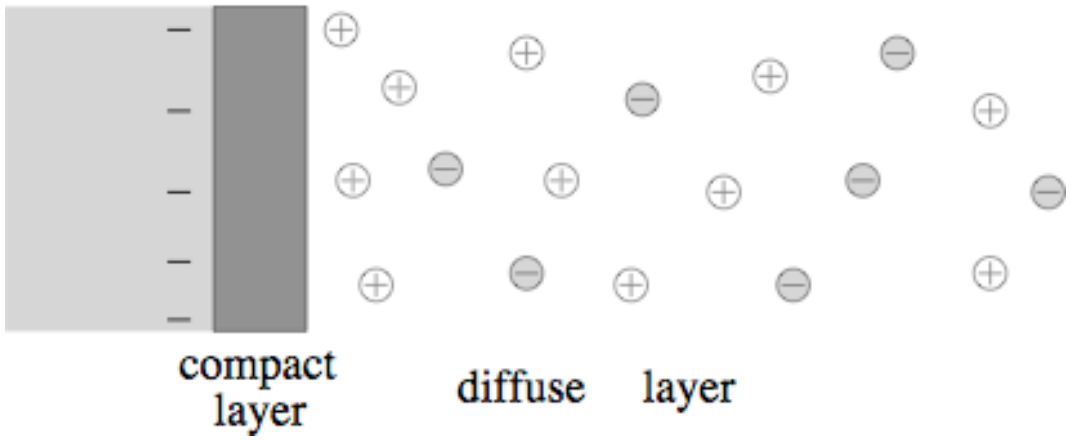
Abstract

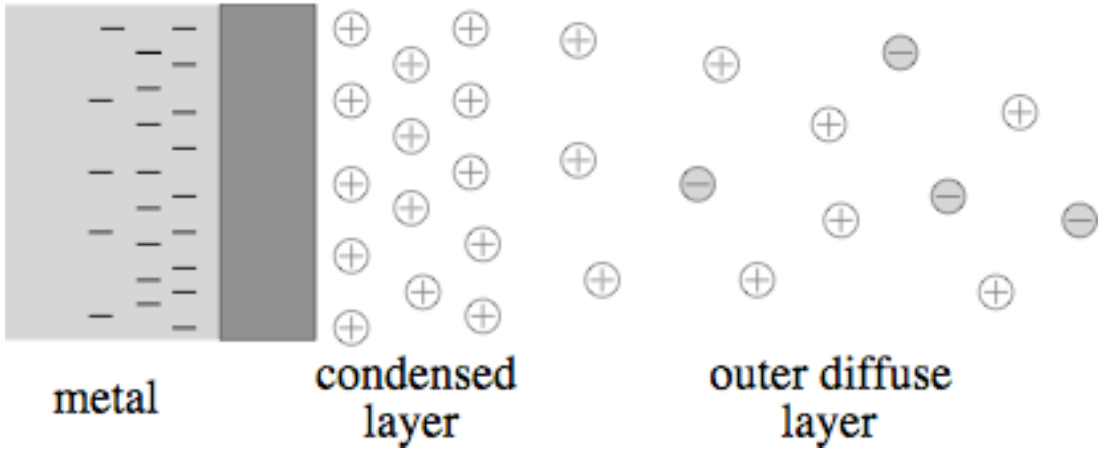
The venerable theory of electrokinetic phenomena rests on the hypothesis of a dilute solution of point-like ions in quasi-equilibrium with a weakly charged surface, whose potential relative to the bulk is of order the thermal voltage ($kT/e \approx 25$ mV at room temperature). In nonlinear electrokinetic phenomena, such as AC or induced-charge electro-osmosis (ACEO, ICEO) and induced-charge electrophoresis (ICEP), several Volts $\approx 100\,kT/e$ are applied to polarizable surfaces in microscopic geometries, and the resulting electric fields and induced surface charges are large enough to violate the assumptions of the classical theory. In this article, we review the experimental and theoretical literatures, highlight discrepancies between theory and experiment, introduce possible modifications of the theory, and analyze their consequences. We argue that, in response to a large applied voltage, the "compact layer" and "shear plane" effectively advance into the liquid, due to the crowding of solvated counter-ions. Using simple continuum models, we predict two general trends at large voltages: (i) ionic crowding against a blocking surface expands the diffuse double layer and thus decreases its differential capacitance, and (ii) a concomitant viscosity increase near the surface reduces the electro-osmotic mobility. The former effect can predict high-frequency flow reversal in ACEO pumps, while the latter may explain the universal decay of ICEO flow with increasing salt concentration. Through several colloidal examples, such as ICEP of an uncharged metal sphere in an asymmetric electrolyte, we predict that nonlinear electrokinetic phenomena are generally ion-specific. Similar theoretical issues arise in nanofluidics (due to molecular confinement) and ionic liquids (due to the lack of solvent), so the paper concludes with a general framework of modified electrokinetic equations for finite-sized ions.

Some crucial new physics:

Ion crowding at large voltages



$$\Psi_D \approx \frac{kT}{ze}$$



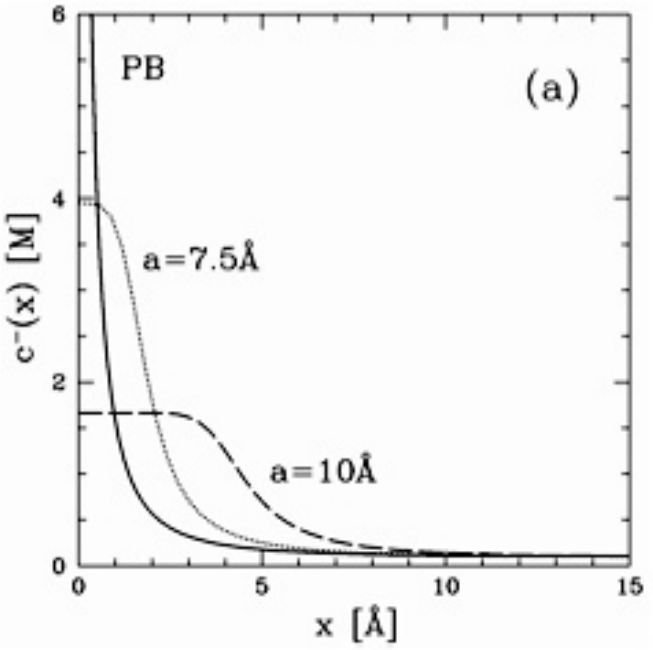
$$\Psi_D \gg \frac{kT}{ze}$$

Finite-sized ions in equilibrium

Modified Poisson-Boltzmann equation

a = minimum ion spacing

JJ Bikerman (1942); Mott & Grimley (1947);
Dutta, Indian J Chem (1949);
Wicke & Eigen, Z. Elektrochem. (1952)
Iglic & Kral-Iglic, Electrotech. Rev. (Slovenia) (1994).
Borukhov, Andelman & Orland, Phys. Rev. Lett. (1997)
Kilic, MZB, Ajdari (2007); Kornyshev (2007); Oldham (2007)



Borukhov et al. (1997)
Large ions, high concentration

- Mean-field electrostatics
- Continuum approx. of lattice entropy ("ideal solution")
- Ignore ion & wall correlations, solvent forces, etc.

$$\varepsilon \nabla^2 \psi = \frac{2zec_0 \sinh\left(\frac{ze\psi}{kT}\right)}{1+2a^3c_0\left[\cosh\left(\frac{ze\psi}{kT}\right)-1\right]}$$

"Fermi-Dirac" statistics

Modified Poisson-Nernst-Planck equations

Kilic, MZB, Ajdari, Phys. Rev. E (2007) — Sudden DC voltage, 1d blocking cell
Olesen, MZB, Bruus, in preparation — AC voltage, 1d cell
Storey, Kilic, Adjari, MZB PRE (2008) — ACEO pumping ("weakly nonlinear")

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \vec{F}_i \qquad \vec{F}_i = c_i \vec{u} - \frac{D_i c_i}{kT} \nabla \mu_i$$

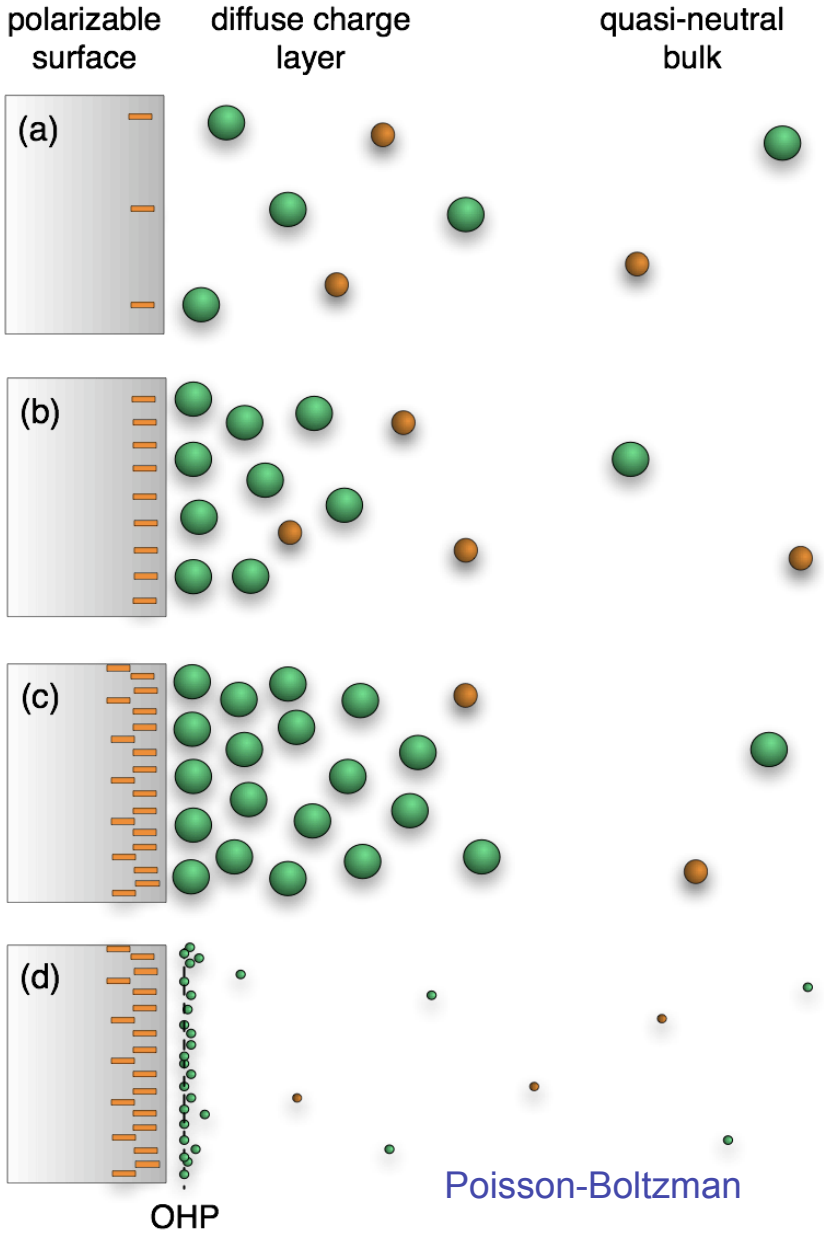
$$\mu_i = \frac{\delta G}{\delta c_i} = z_i e \psi + kT \log \nu_i c_i + \mu_i^{ex}$$

$$-\nabla \cdot (\varepsilon \nabla \psi) = \sum z_i e c_i$$

Excess electro-chemical potential, e.g. volume constraints:

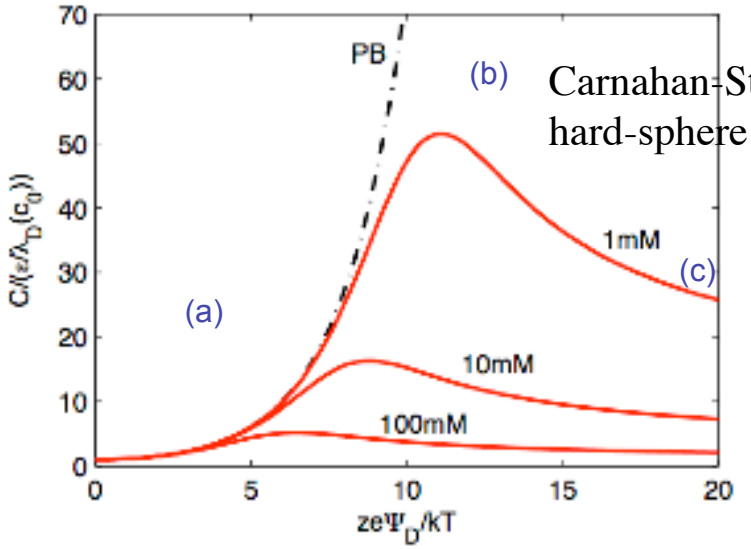
$$\frac{\mu_i^{ex}}{kT} = \begin{cases} 0 & \text{dilute solution} \quad \text{PNP} \\ -\log(1-\Phi) & \text{lattice gas} \quad \text{Bikerman} \\ \frac{\Phi(8-9\Phi+3\Phi^2)}{(1-\Phi)^3} & \text{hard spheres} \quad \text{Carnahan-Starling} \\ \ldots. & \ldots \end{cases}$$

Effect 1. Dynamical Ion Crowding



Poisson-Boltzman

1. Salt adsorption & surface conduction reduced (Du)
2. Differential capacitance *decays* at large voltage



-Analytical formula, lattice gas

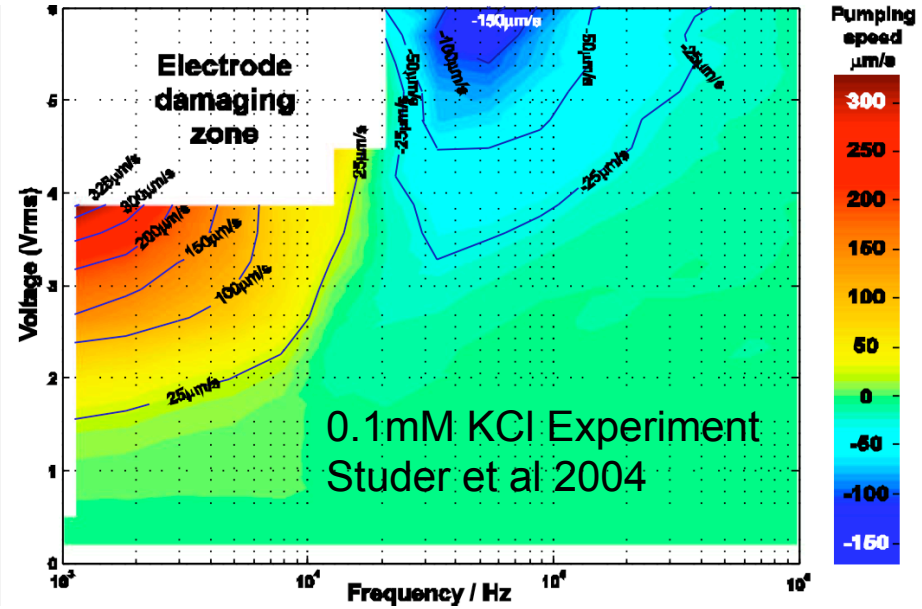
Freise 1952, Kilic et al 2007, Kornyshev 2007

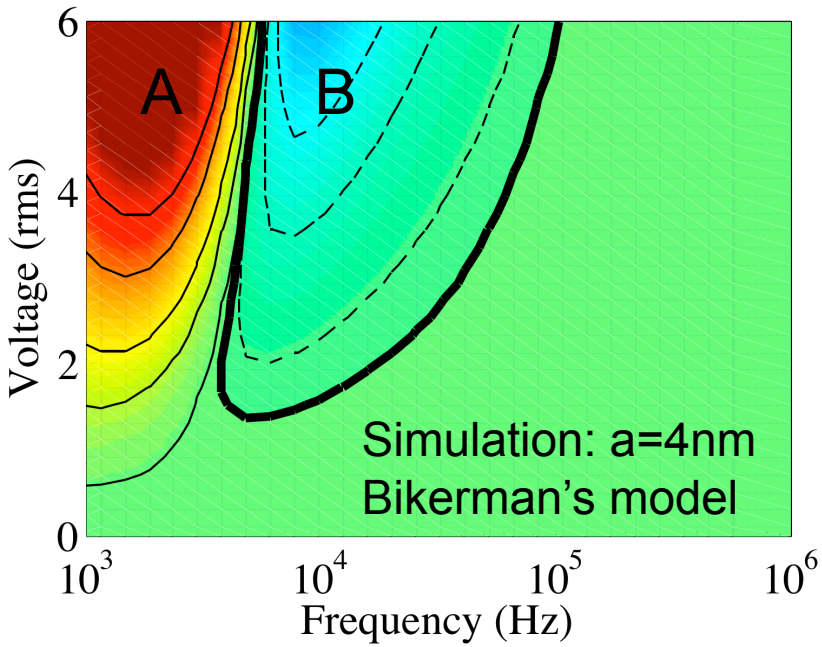
-Hard-sphere liquid models

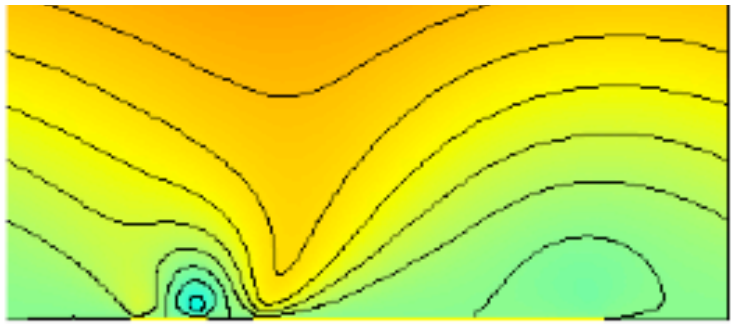
Lue 1997, Dicaprio 2003

A theory of high-freq. ACEO flow reversal

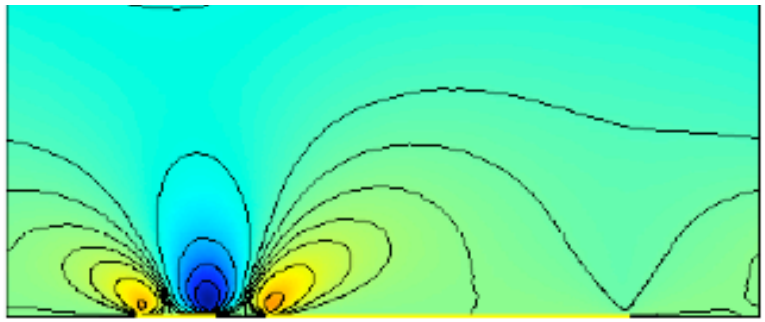
Storey, Edwards, Kilic & Bazant, Phys. Rev. E (2008)





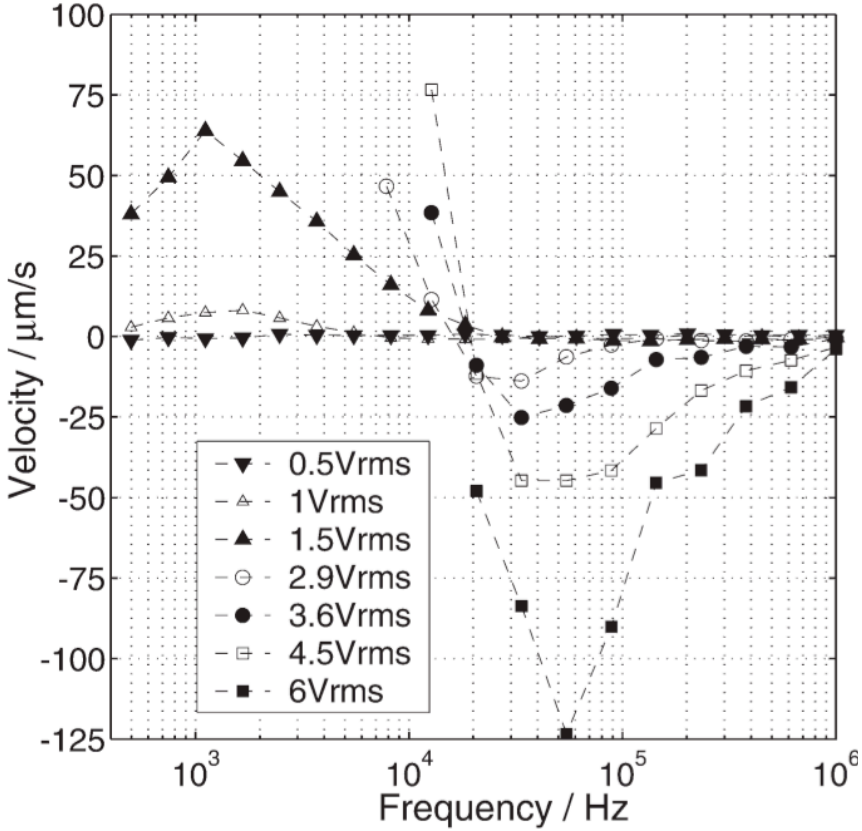


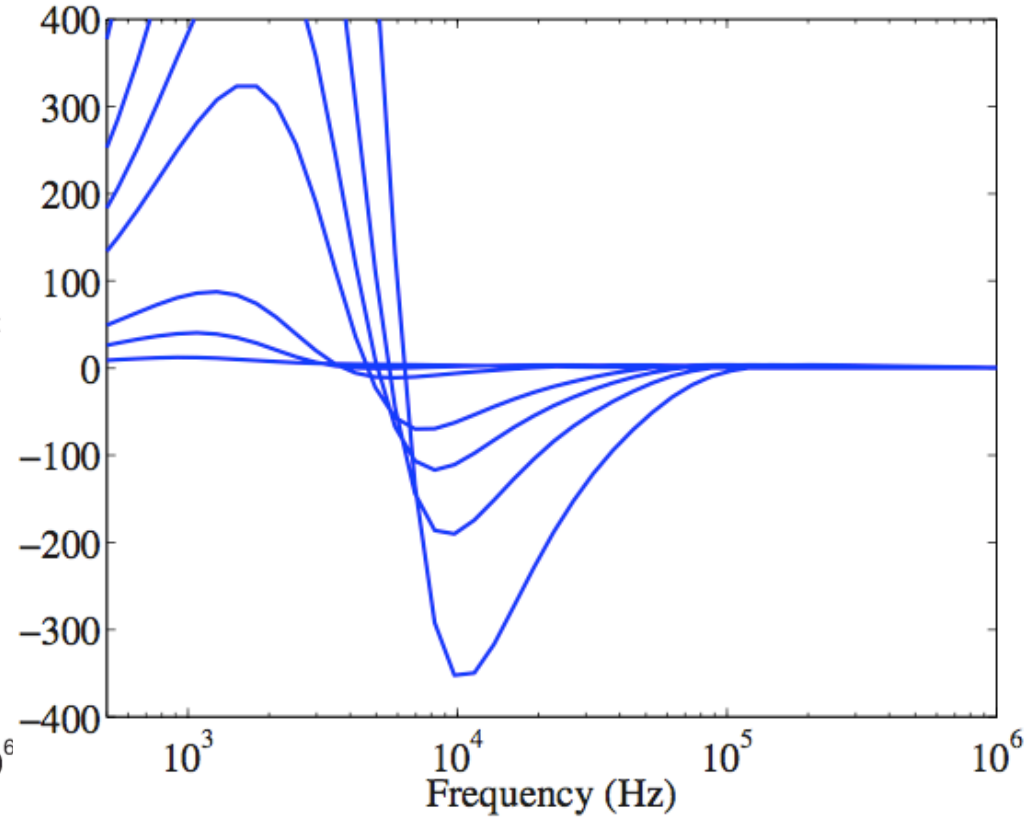
A. Large electrode wins



B. Small electrode wins

Planar ACEO Flow Reversal





Experiment: Studer et al (2004)
0.1mM KCl
Microfluidic loop
Brown et al planar design

Theory: Storey et al (2008)
Bikerman's lattice-gas model a=4.4nm !
Similar for hard spheres (CS), a=2.2nm
Variable permittivity, can use a=1nm

What is the “ion size”?

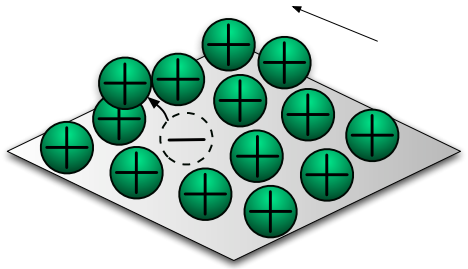
Ion	d_x (Å)	d_s (Å)	d_v (Å)
Li^+	1.20	7.64	4.2
Na^+	1.90	7.16	4.0
K^+	2.66	6.62	3.8
Cl^-	3.62	6.64	3.6

- d_x=in crystal, d_s=“solvated”, d_v= Stokes radius from viscosity

- Maybe larger for a charged “Wigner glass” of only counter-ions due to <u>electrostatic correlations</u> (beyond the mean-field approximation)

$$l_B = \frac{e^2}{4\pi\varepsilon kT} = 7\text{Å}, \quad \varepsilon = 80\varepsilon_0$$
$$= 7\text{nm}, \quad \varepsilon = 8\varepsilon_0$$

Bjerrum length



“correlation hole”

Can we fit electrochemical data?

Yes, for interfaces without specific adsorption of ions, but with a large "ion size" – the same used to fit ACEO!

Sabri Kilic, PhD thesis, 2008

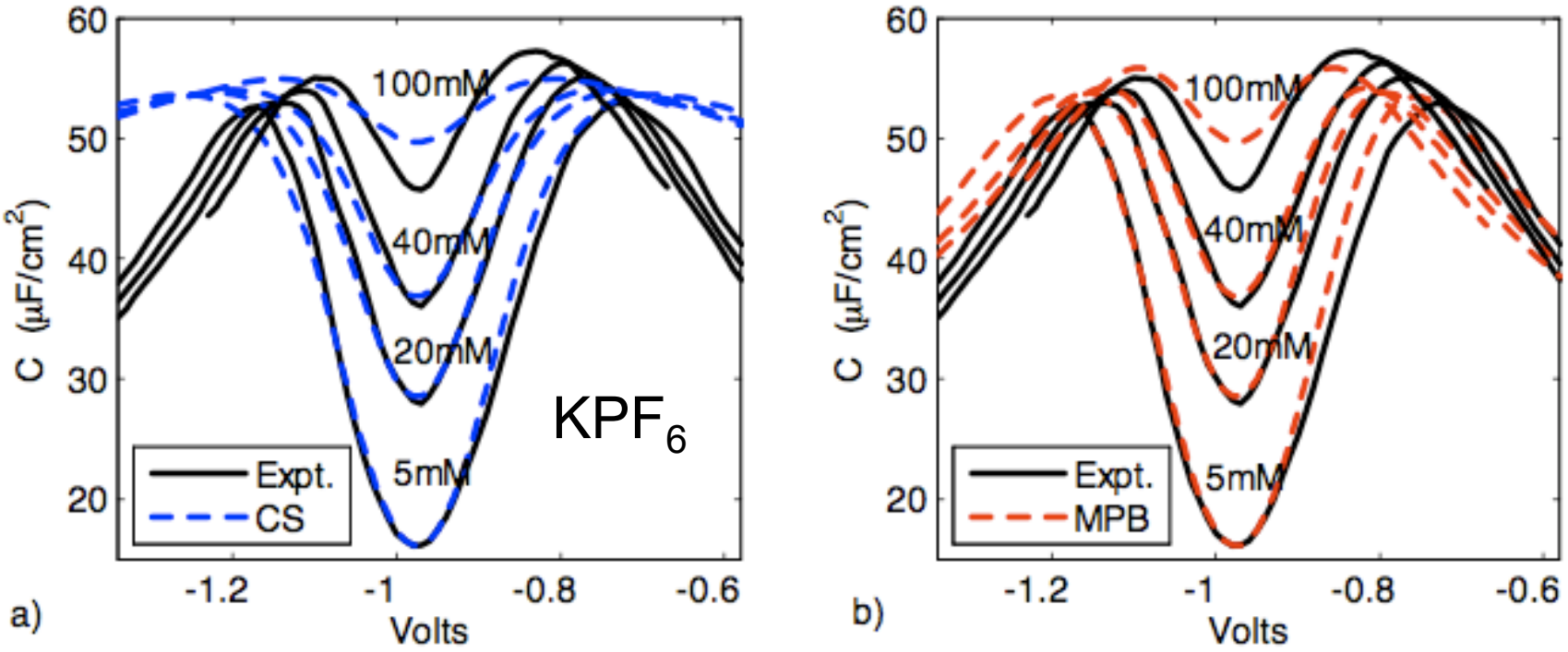
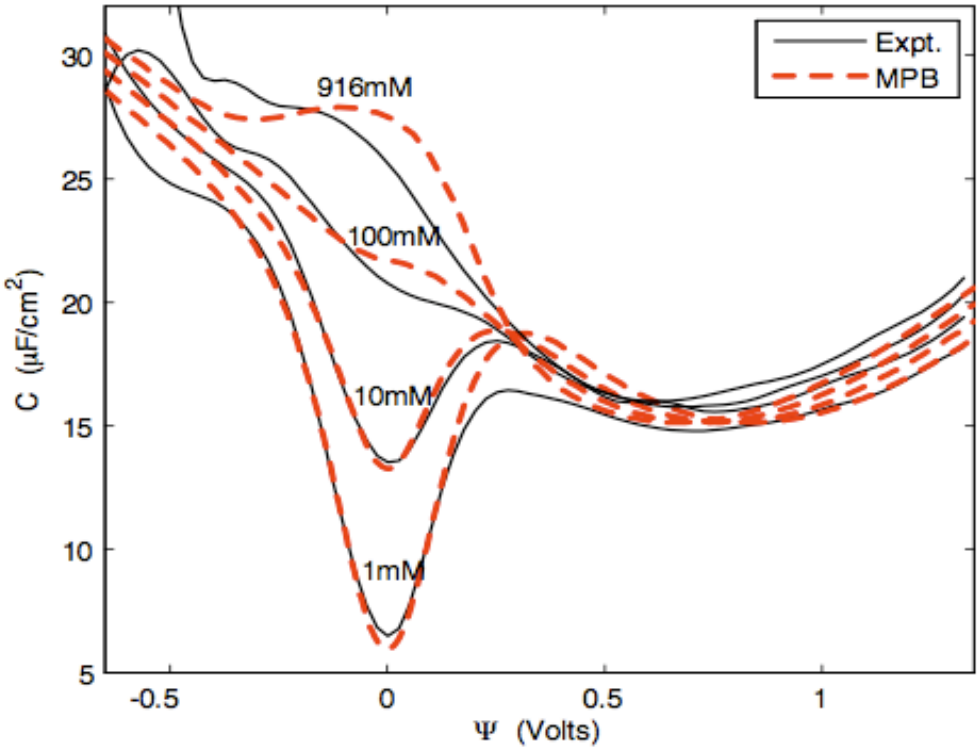


Figure E-5: Differential capacitance data in Fig.3 of [181] is fitted by (a) CS model (b) the MPB model. The effective ion diameter is taken to be $a = 4A$ for the CS model, whereas the size of ions is $a = 11A$ for the MPB model.

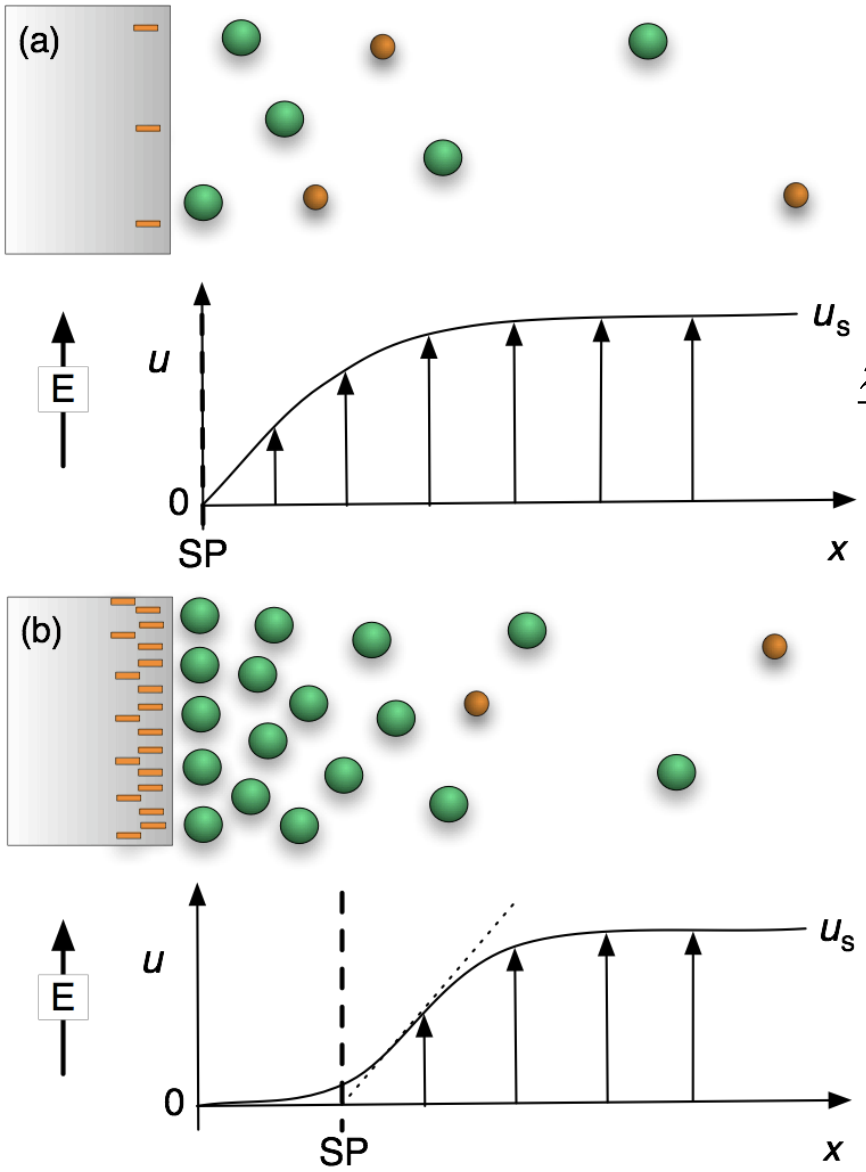
Grahame's famous 1948 electrocapillary data for NaCl / Mercury drop, fitted by Bikerman + a specific adsorption model



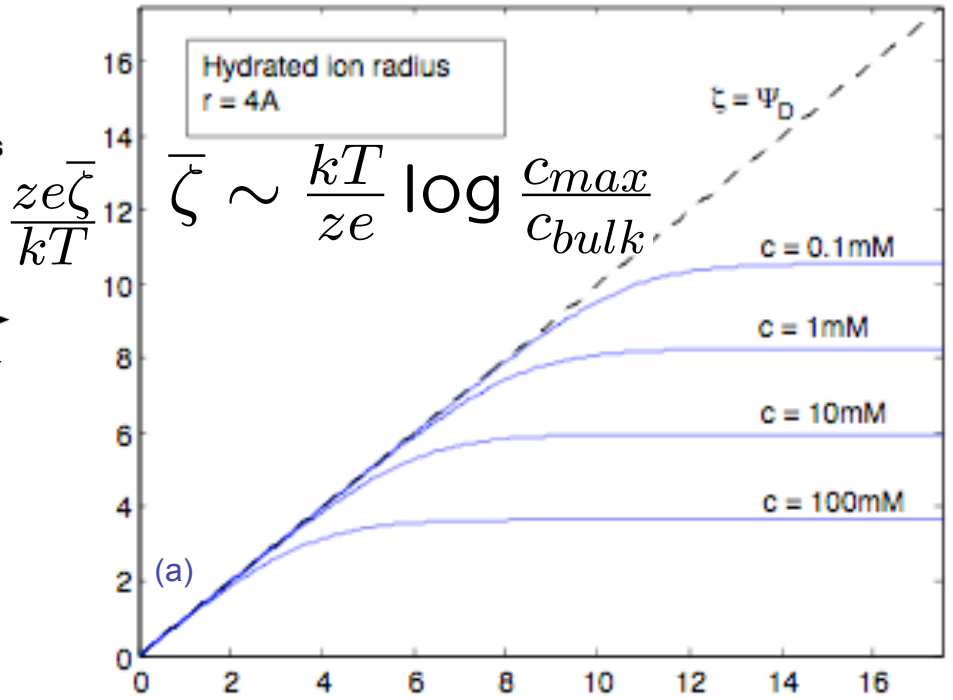
Sabri Kilic thesis 2008, with Antonio Ramos, MIT-Spain grant

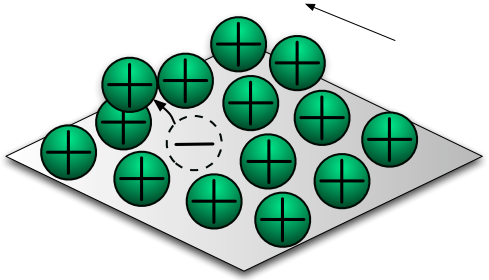
Figure F-2: Differential capacitance data from Grahame [72] for NaF at room temperature is fitted by the specific adsorption model using the MPB steric model. Note that all other parameters are kept constant for different bulk concentrations.

Effect 2. Charge-induced thickening



Electro-osmotic mobility (zeta) saturates at large V





Possible mechanism:
“sheared Wigner glass”

Modified Helmholtz-Smoluchowski formula

Bazant, Kilic, Ajdari (2006-2009).

Electro-osmotic mobility for variable viscosity and/or permittivity:

$$\frac{u_s}{E_t} = \frac{\varepsilon_0 \overline{\zeta}}{\eta_0} = \int_0^{\Psi} \frac{\varepsilon}{\eta}\, d\psi$$

1. Lyklema, Overbeek (1961): viscoelectric effect $\quad \dfrac{\Delta\eta}{\eta_0} = f E^2$

2. Instead, we assume viscosity diverges at maximum charge density

$$\frac{\varepsilon}{\eta} = \frac{\varepsilon_0}{\eta_0}\left(1 - \left|\frac{\rho}{\rho^{\pm}_{max}}\right|^{\alpha}\right)^{\beta}$$

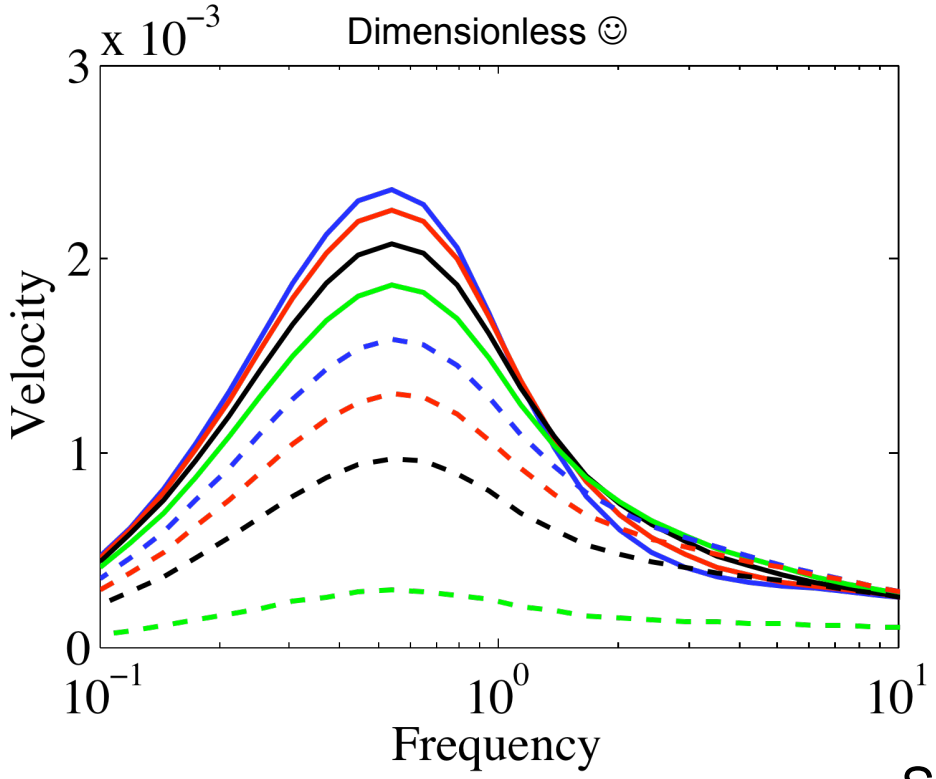
Modified slip formula $\quad \alpha = \beta = 1 \quad$ (can use for any MPB theory)

$$\overline{\zeta} = \Psi - \mathrm{sgn}(\Psi)\frac{q(\Psi)^2}{2\varepsilon\rho_{max}}$$

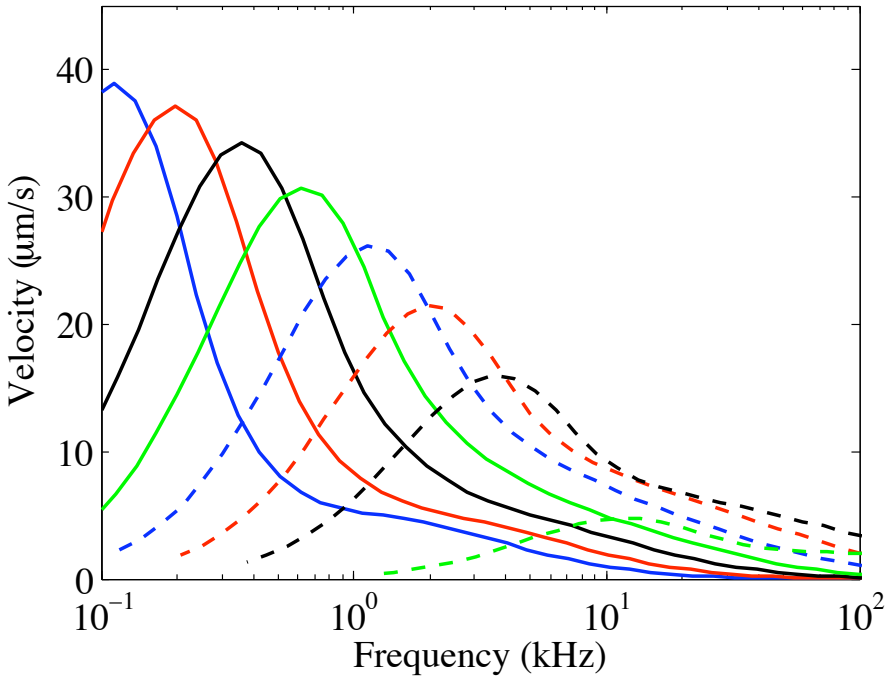
Theory of ACEO concentration dependence (?)

Bazant, Kilic, Storey & Ajdari, New J Phys & ACIS (2009)

Dimensionless ☺



With dimensions from our expts ☹



Postulate:

$$\frac{\varepsilon}{\eta} = \frac{\varepsilon_b}{\eta_b}\left(1 - \frac{a^3|\rho|}{ze}\right)$$

Simulation:

-Bikerman MPB (a=4nm)

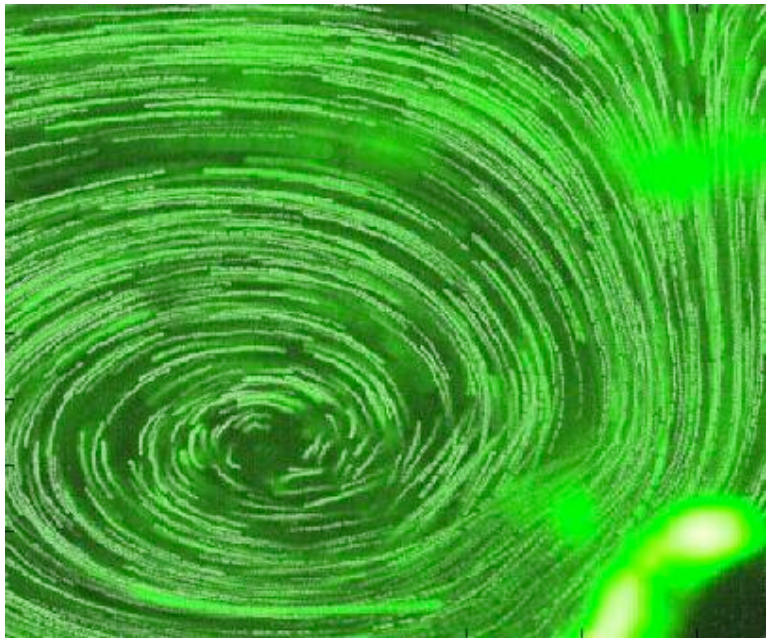
-Diverging viscosity at close packing

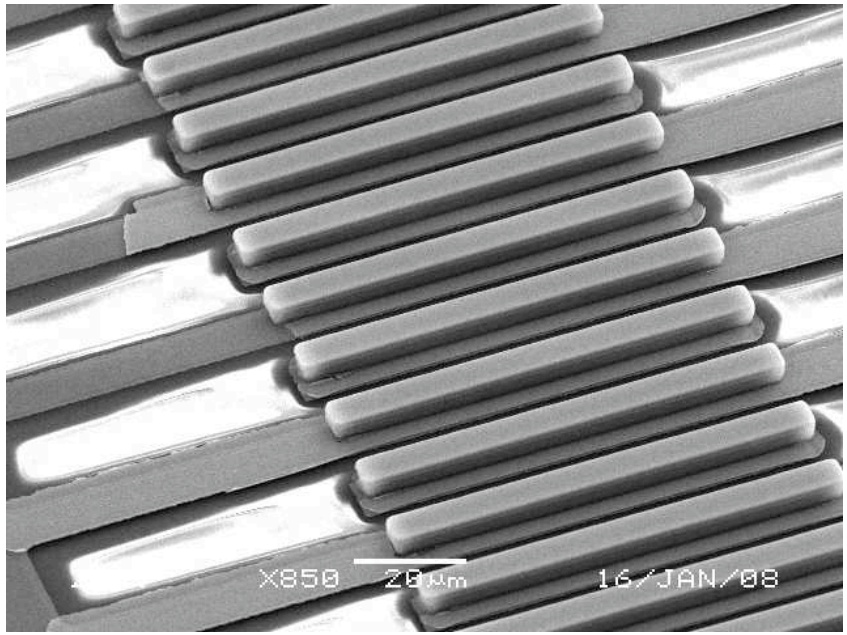
-No new parameter, only the cutoff size!

-Fits conc. decay, but loses reversal

Conclusion

Induced-charge / AC electrokinetics is a frontier of theoretical physics and applied mathematics with many possible applications in microsystems.





Papers, slides: http://web.mit.edu/bazant/www