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Electrokinetics and Electrohydrodynamics of Microsystems

Induced-Charge Electrokinetic Phenomena

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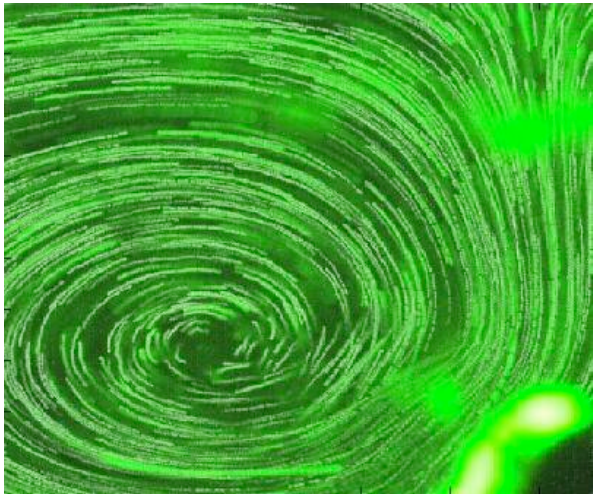
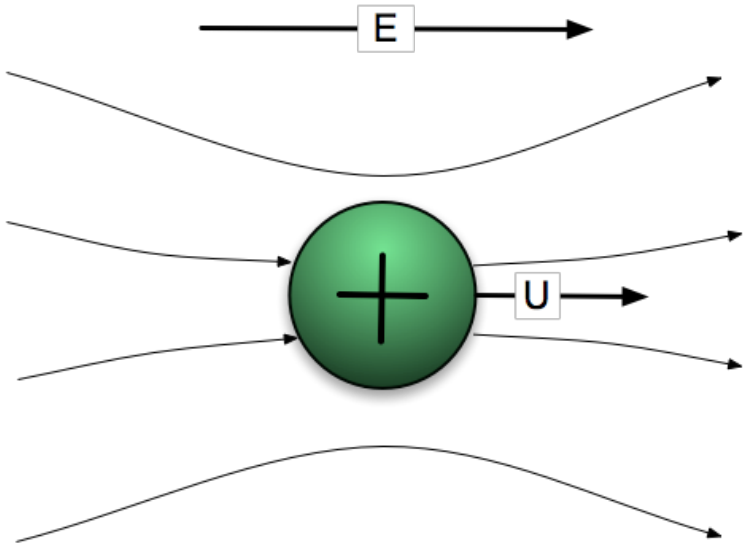
Lectures

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



Background:
Linear Electrophoresis

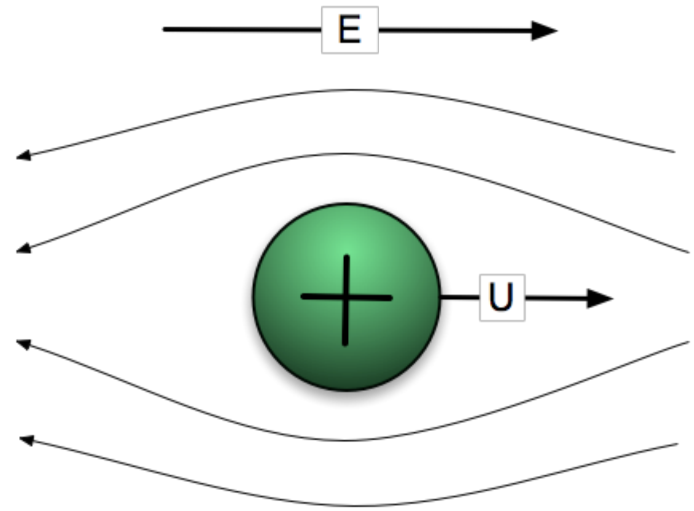
Electrophoresis in a dielectric liquid



Lab frame

$$U = \frac{qE}{6\pi\eta R}$$

Size-dependent velocity



Particle frame

$$u \sim \frac{R}{r}$$

Long-range flow perturbation

Electrophoresis in an electrolyte

Smoluchowski (1907)

Electro-osmotic slip

$$u_s = -\mu_e E_t$$

Electrophoretic mobility

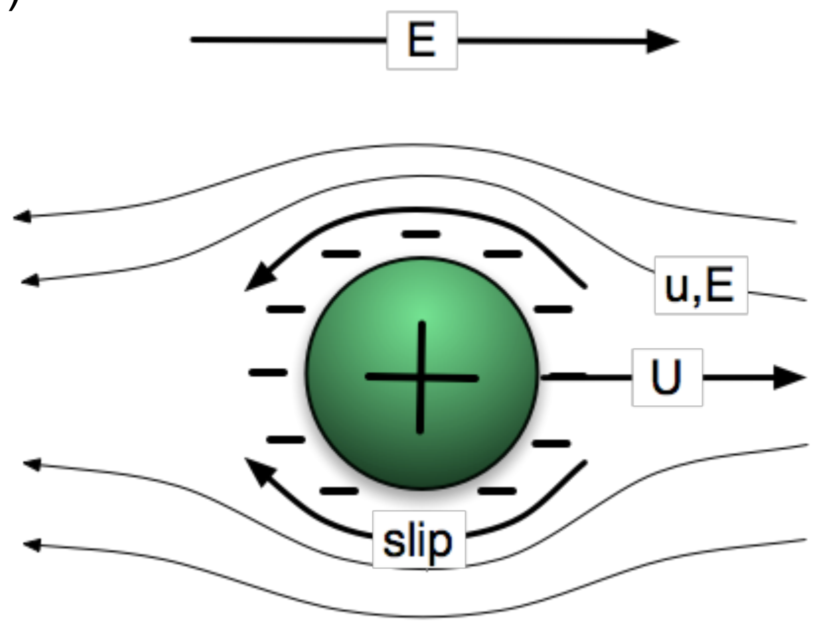
$$\mu_e = \frac{\varepsilon\zeta}{\eta}$$

Zeta potential

$$\zeta = \Delta\phi_D = q/C_D$$

Size-independent velocity

$$U = \mu_e E_\infty$$



force-free motion

$$u \sim \left(\frac{R}{r}\right)^3$$

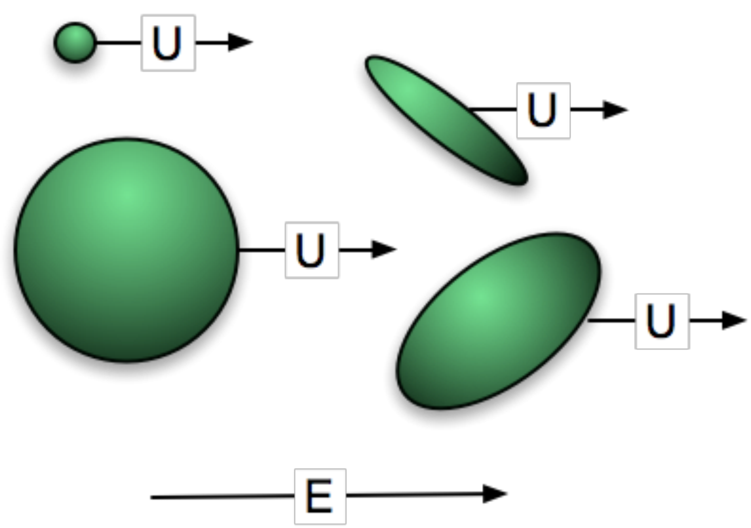
short-range flow perturbation

Electrophoresis of colloids

Morrison (1970) – thin double layers; uniform, small surface charge

$$\nabla^2 \phi = 0, \ \vec{E} = -\nabla\phi, \ \hat{n}\cdot\vec{E} = 0$$
$$\nabla^2 \vec{u} = \nabla p, \ \nabla\cdot\vec{u} = 0, \ \hat{n}\cdot\vec{u} = 0$$

$$\vec{u}_s = -\mu_e \vec{E}_t$$



Solution for uniform mobility: potential flow

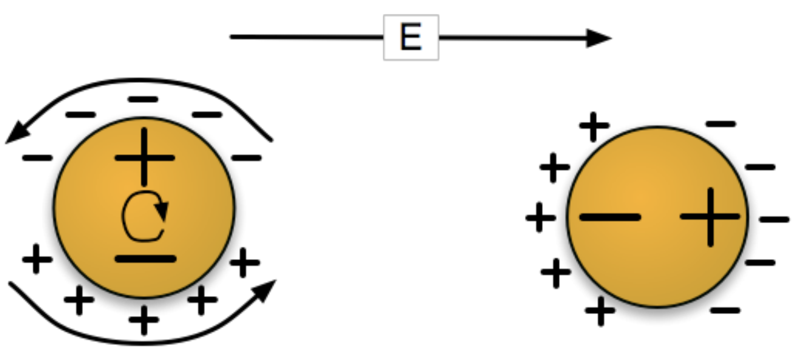
$$\vec{u} = -\mu_e \vec{E}, \ p = 0$$
$$\vec{U} = \mu_e \vec{E}_\infty$$

Zero relative motion!

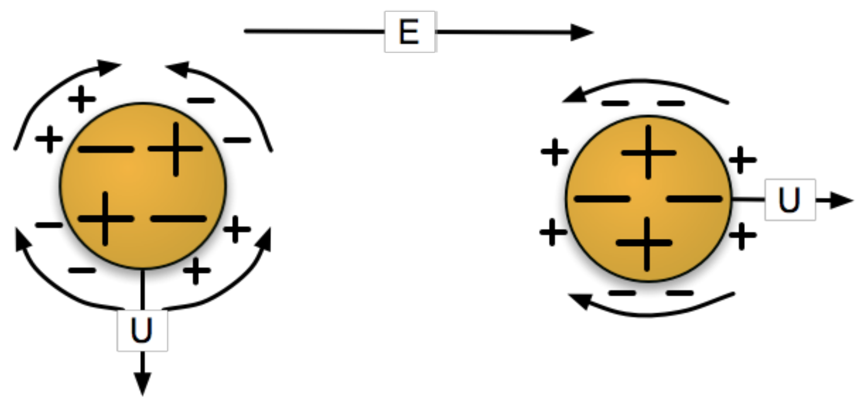
Heterogeneous Particles

Anderson 1984; Ajdari 1995, Long & Ajdari 1998

An inhomogeneous sphere rotates to align dipole with *E*. Electrophoresis enhances forced electro-rotation.



Transverse EP is possible, for certain orientations



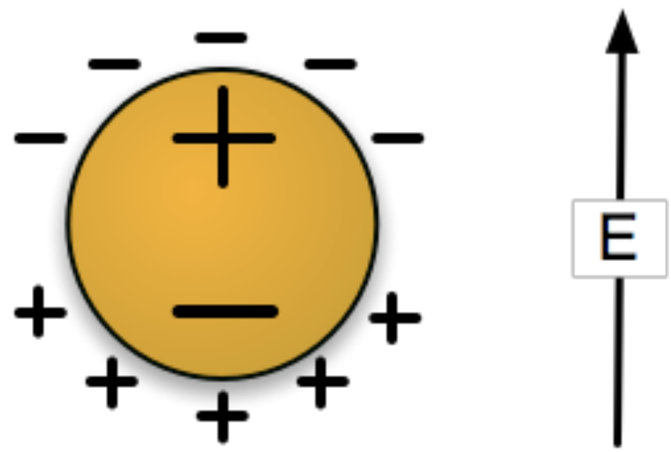
EP mobility is not related to total or average charge!

Non-spherical AND inhomogeneous particles can rotate along one axis or exhibit transverse EP in all orientations.

Nonlinear “induced-charge” electrophoresis of polarizable homogeneous particles

Electrophoresis of **Polarizable** Particles

Classical result, e.g. Levich (1956):
Electrophoretic mobility depends on the total charge, but not on the induced dipole moment



Induced dipole

…BUT this only holds for linear response to small E

Stotz-Wien-Dukhin Effect

For nonlinear double-layer capacitance, the mobility depends on E, since induced charge must redistribute to maintain the same the total charge (AS Dukhin 1992)

$$\mu_e(E) \sim \frac{\varepsilon}{\eta}\left(\zeta - \frac{3}{8}\frac{C'(\zeta)}{C(\zeta)}(ER)^2 + \ldots\right)$$

Can exploit for separation in “unbalanced” AC fields

$$\langle E \rangle = 0, \quad \text{but} \quad \langle E^3 \rangle \neq 0$$

(SS Dukhin et al 1986, R Chimenti, patent 1986)

Ion-specific mobility

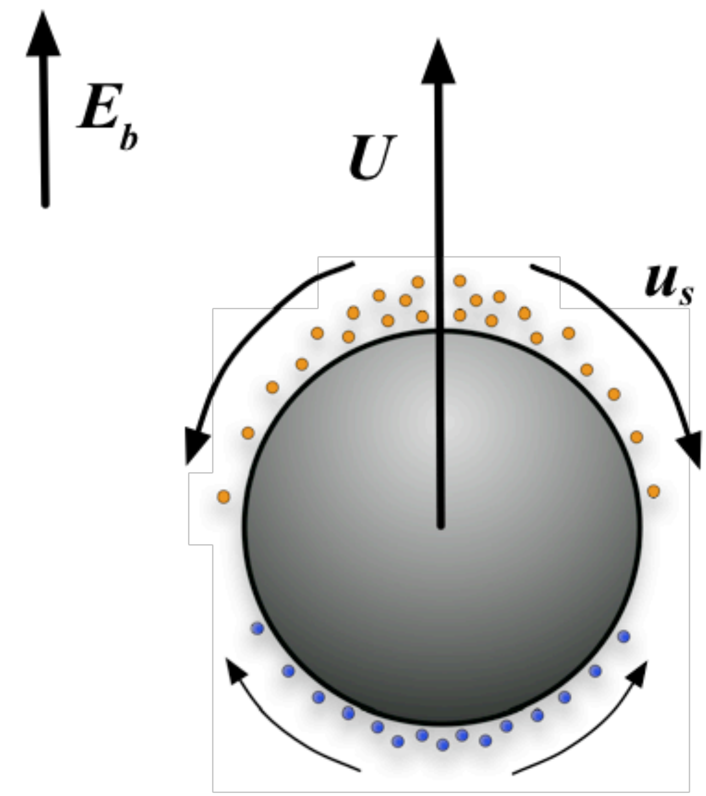
Bazant, Kilic, Storey, Ajdari, Adv Coll Interface Sci (2009)

Dukhin effect in an *asymmetric electrolyte*

Mobility must also depend on ion charges, sizes, etc.

Even an *uncharged sphere* can move, if it is polarizable

Its apparent charge is that of ions which screen at higher density



Dielectrophoresis (DEP)

Maxwell-Wagner induced dipole moment

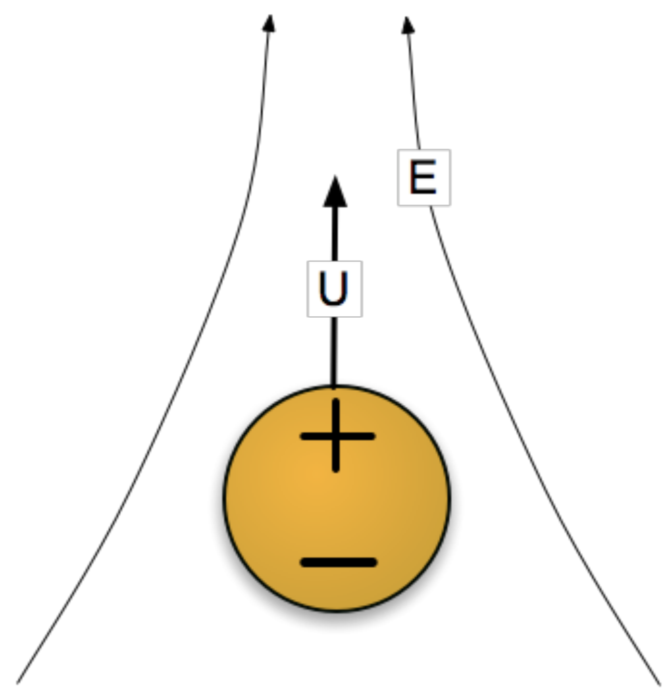
$$p = 4\pi\varepsilon \left(\frac{\sigma_p - \sigma + i\omega(\varepsilon_p - \varepsilon)}{\sigma_p + \sigma + i\omega(\varepsilon_p + \varepsilon)} \right) R^3 E$$

Time-averaged force and torque

$$\begin{aligned} \langle \vec{F} \rangle &= (\text{Re } \vec{p}) \cdot \nabla \vec{E} \\ \langle \vec{T} \rangle &= (\text{Re } \vec{p}) \times \vec{E} \end{aligned}$$

Velocity in Stokes flow

$$\vec{U} = \frac{\langle F \rangle}{6\pi\eta R} \sim \frac{\varepsilon R^2 \nabla E^2}{\eta}$$



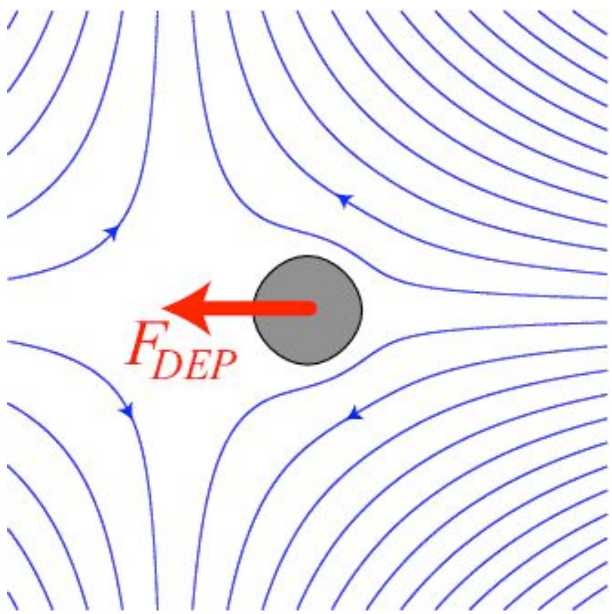
"Dipolophoresis" = DEP + ICEP

Shilov & Simonova, Colloid J. USSR (1981, 2001). Metal sphere dipolophoresis
Squires & Bazant, J. Fluid Mech. (2006). General problem of DEP + ICEP
T. Miloh, Phys. Fluids (2008) Thick DL dipolophoresis theory

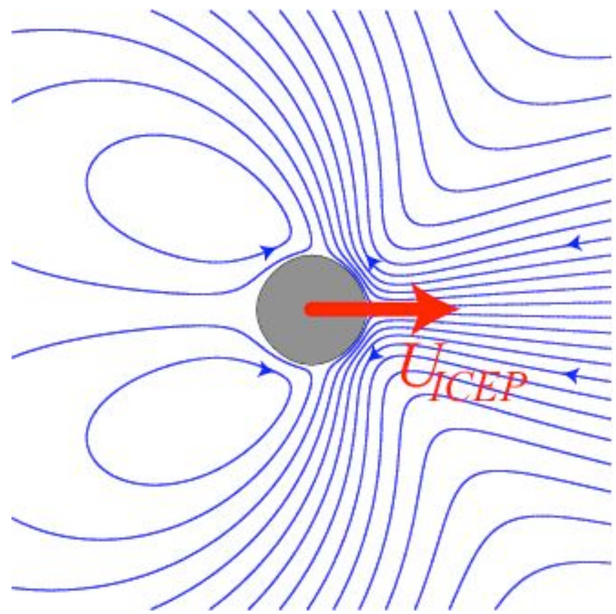
- In an electrolyte, "induced-charge electrophoresis" opposes DEP
- Both effects have the same scaling (and cancel for a metal sphere).

$$U_{ICEP} \sim -U_{DEP} \sim \frac{\varepsilon R^2}{\eta} \nabla |E|^2$$

$\nabla |E| \parallel E$

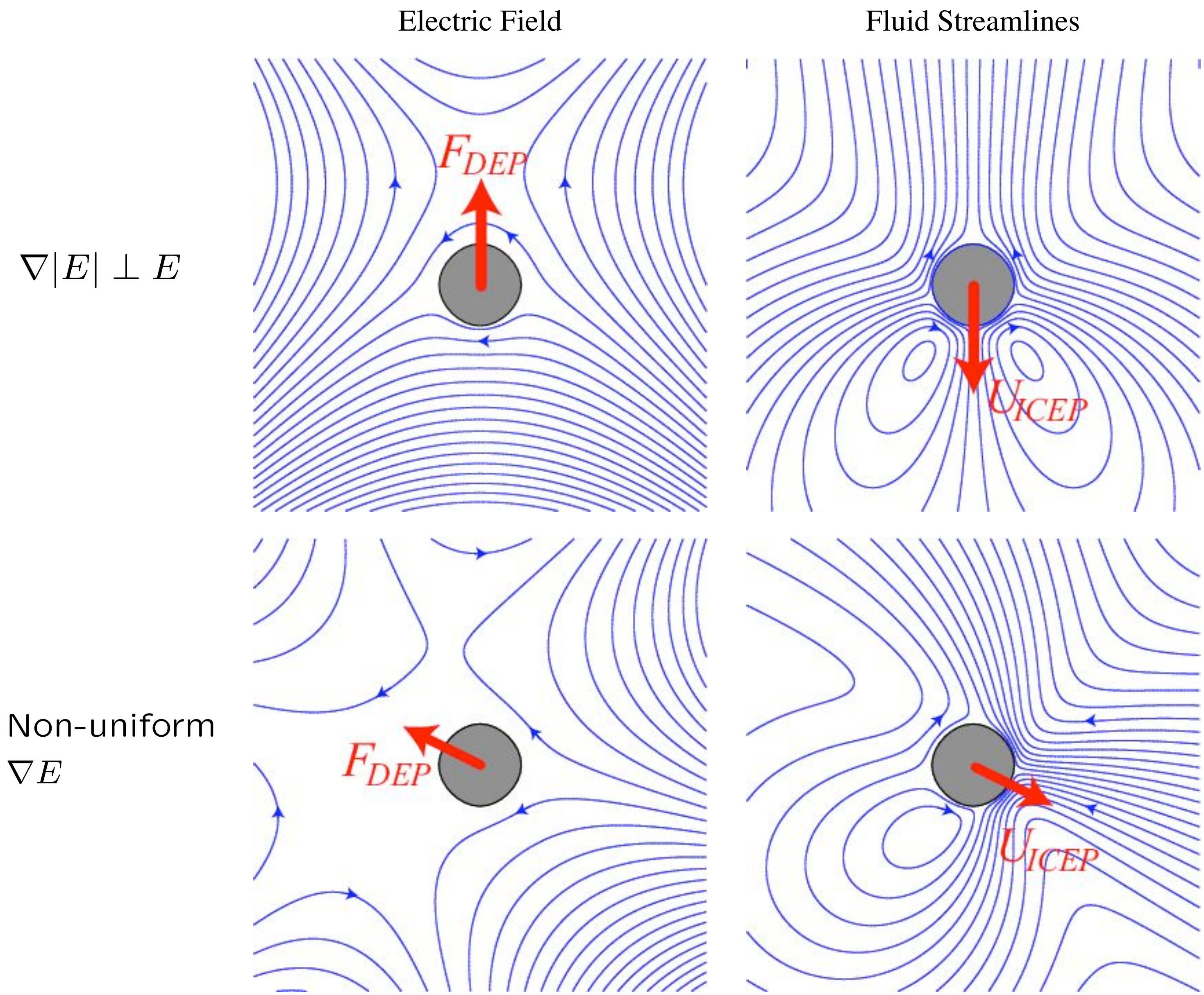


Electric Field



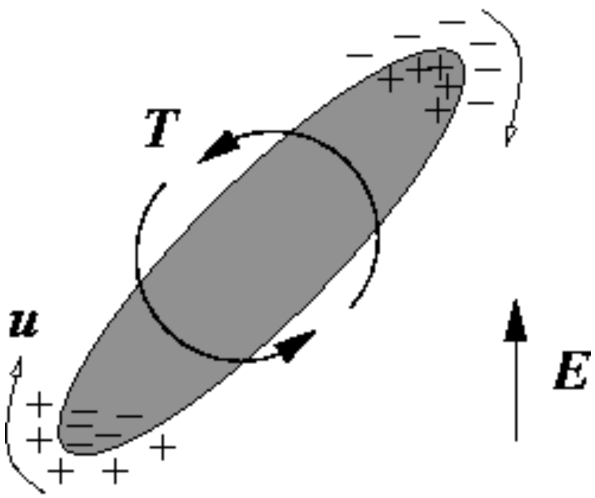
Fluid Streamlines

General solution for any 2d shape in any non-uniform E field by ***complex analysis***…



Induced-charge electrophoresis of *heterogeneous* particles

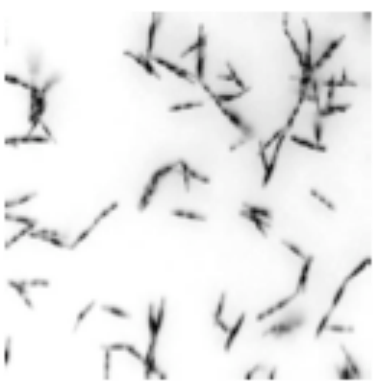
Electrokinetic motion of rod-like metal particles



Perturbation theory:
Squires & Bazant, JFM (2006)

$$\Omega_{ICEP} \sim \frac{\varepsilon R E^2}{\eta}$$

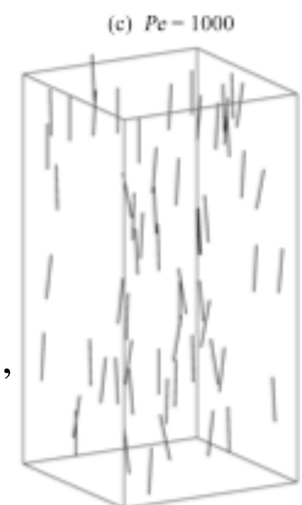
$$\sim p \times E = T_{DEP}$$



Field off

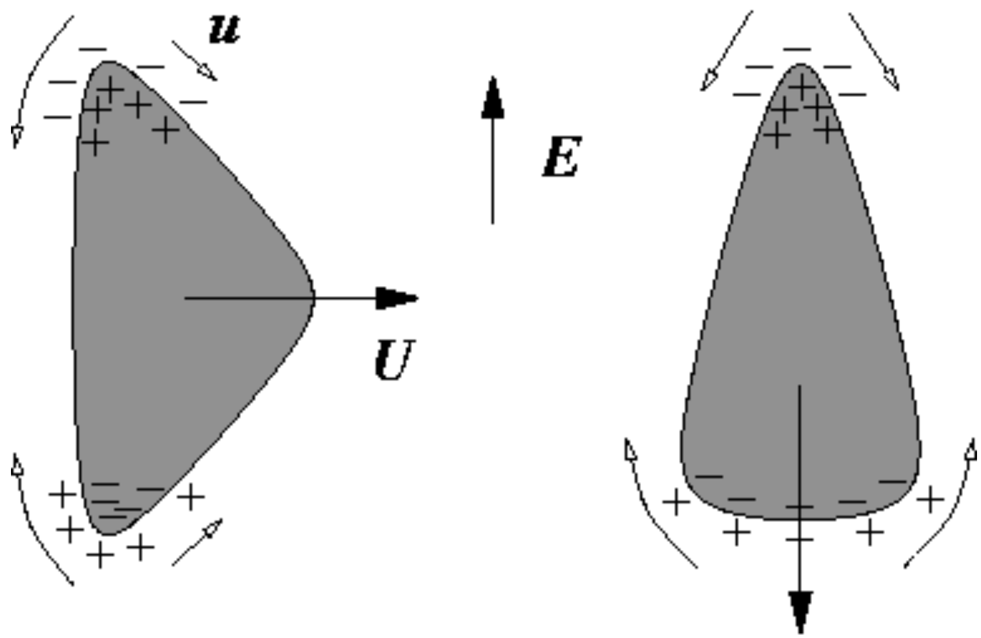
Field on

Rose & Santiago,
Phys Rev E (2006):
Experiments on alignment
of "nano-barcode" particles



Saintillan, Darve & Shaqfeh,
J Fluid Mech (2006): theory
for spheroids + simulations

ICEP of Irregular Shapes

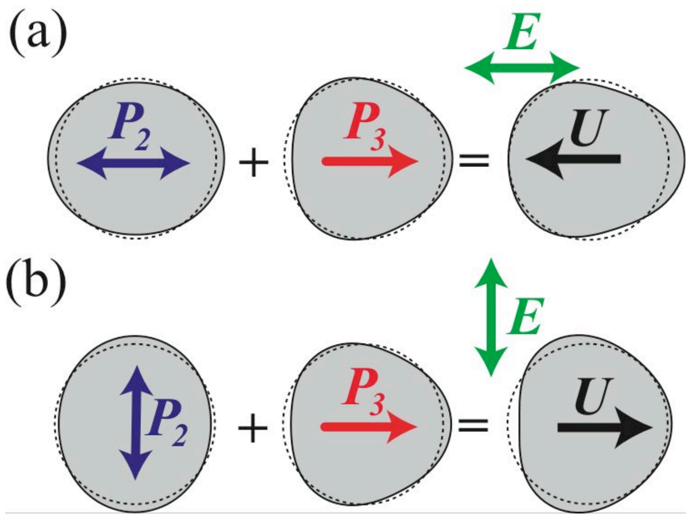


ICEP can separate particles of the same material and same size by shape alone. Any direction is possible.

Expts on quartz particles: Gamayunov & Murtsovkin (1992). Theory: Bazant & Squires (2004)
Tensor relations: Yariv (2005); Perturbation analysis: Squires & Bazant (2006).

ICEP of Asymmetric Shapes

Squires & Bazant, J. Fluid Mech. (2006).

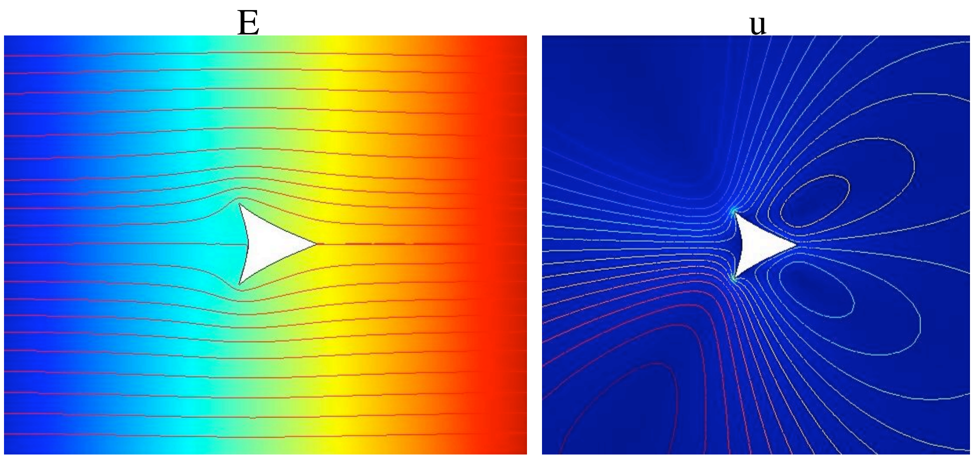


Perturbation analysis

ICEP can separate polarizable colloids by shape and size in a uniform DC or AC electric field, while normal (linear) electrophoresis cannot.

- long axis rotates to align with E
- a "thin arrow" swims parallel to E, towards its "blunt" end
- a "fat arrow" swims transverse to E towards its "pointed" end

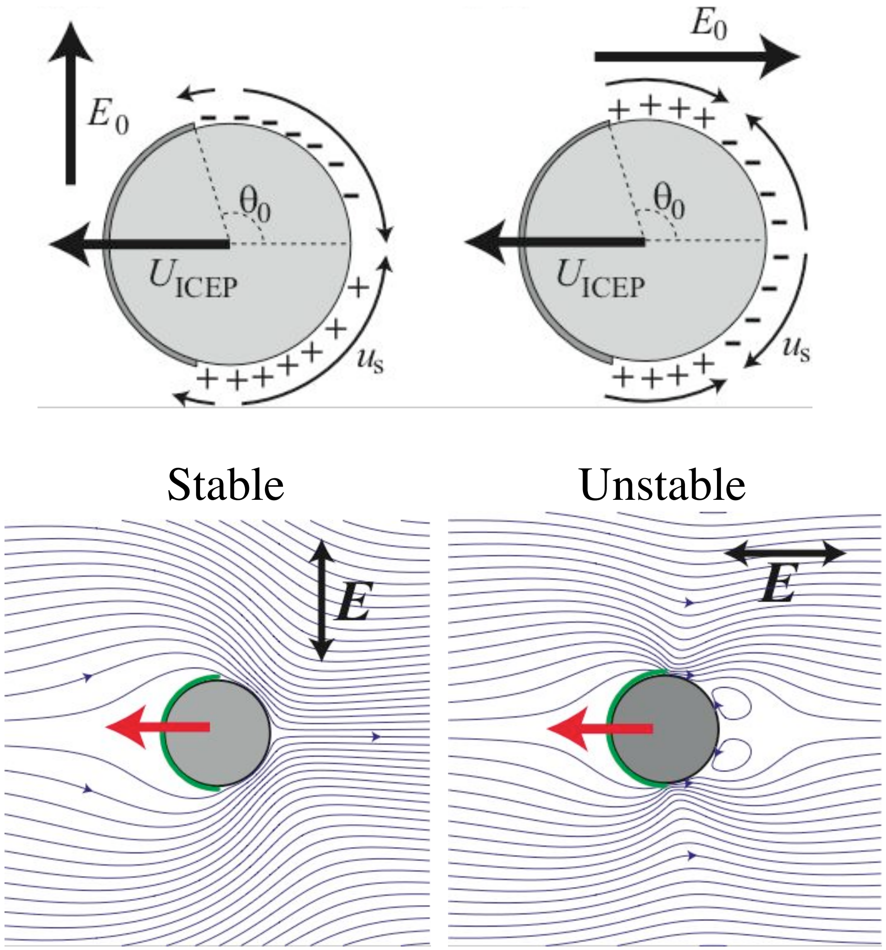
An asymmetric metal post *can pump fluid in any direction* in a uniform DC or AC field, but ICEO flow has quadrupolar rolls, very different from normal EOF.



FEMLAB finite-element simulation (Yuxing Ben)

ICEP of Inhomogeneous Particles

Bazant & Squires, Phys. Rev. Lett. (2004); Squires & Bazant, J. Fluid Mech (2006)



Example: Janus particle

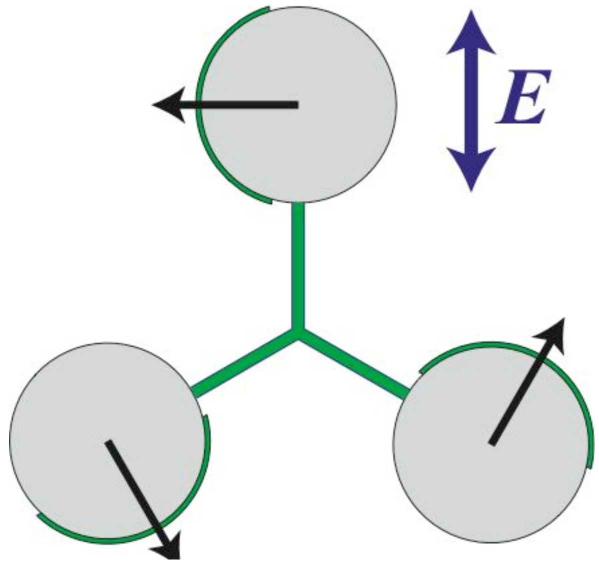
A metal/dielectric sphere in a uniform E field always moves toward its dielectric face, which rotates to perpendicular to E.

The particle swims sideways.

$$U = \frac{9}{64}\frac{\varepsilon a E^2}{\eta}$$

An even more surprising example (Squires & Bazant J Fluid Mech 2006):

An Electrophoretic Pinwheel



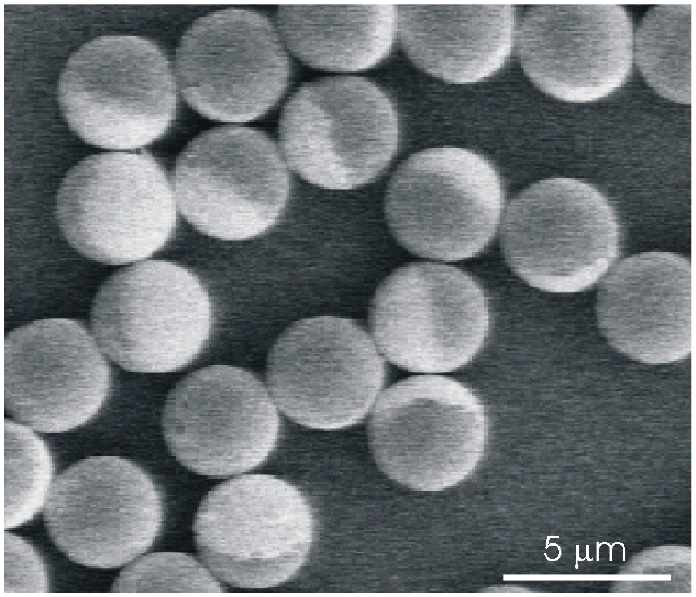
- Responds to <u>any</u> electric field by rotating ($\vec{\Omega} \perp \vec{E}$)
- Could be used to apply torques to molecules or cells?

ICEP Experiments

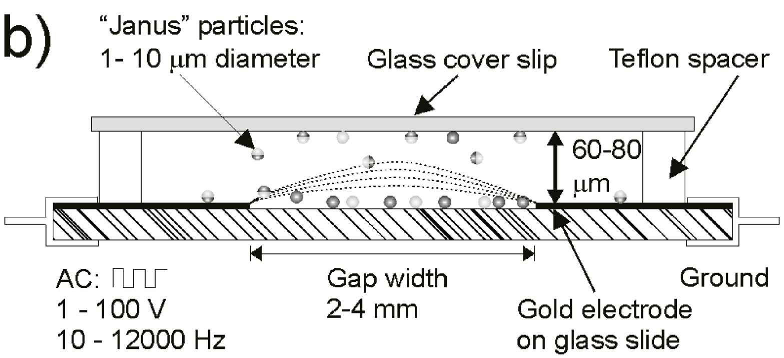
S. Gangwal, O. Cayre, MZB, O.Velev, Phys Rev. Lett (2008).

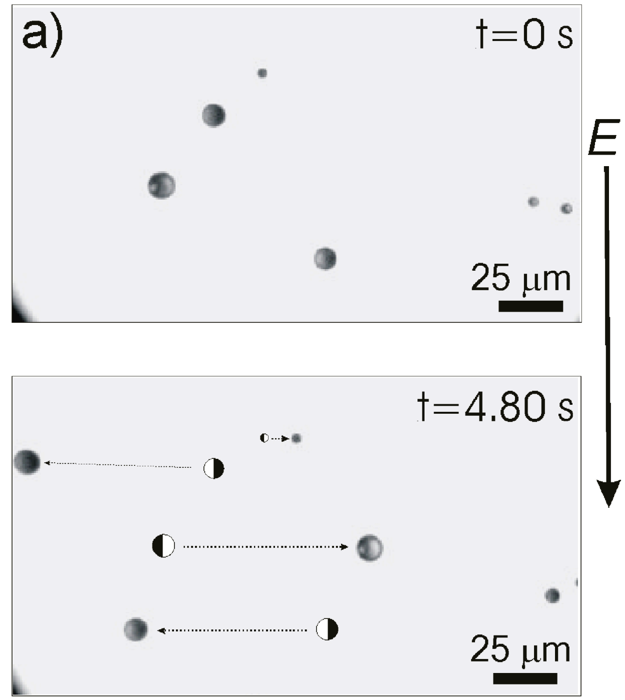
Gold/latex Janus spheres in NaCl

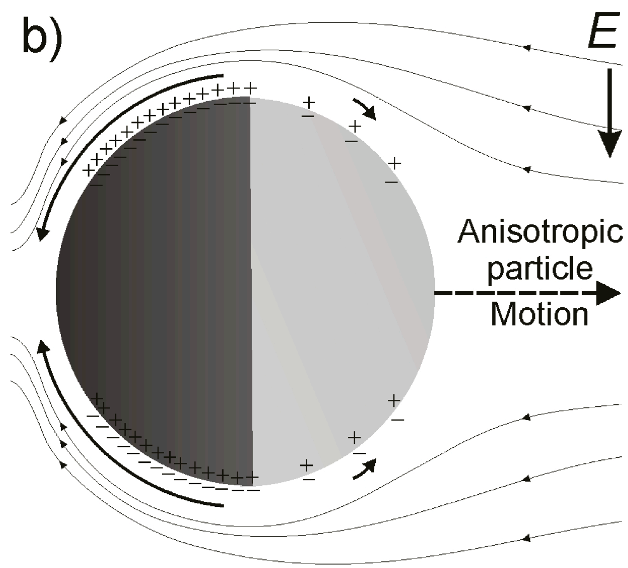
a)



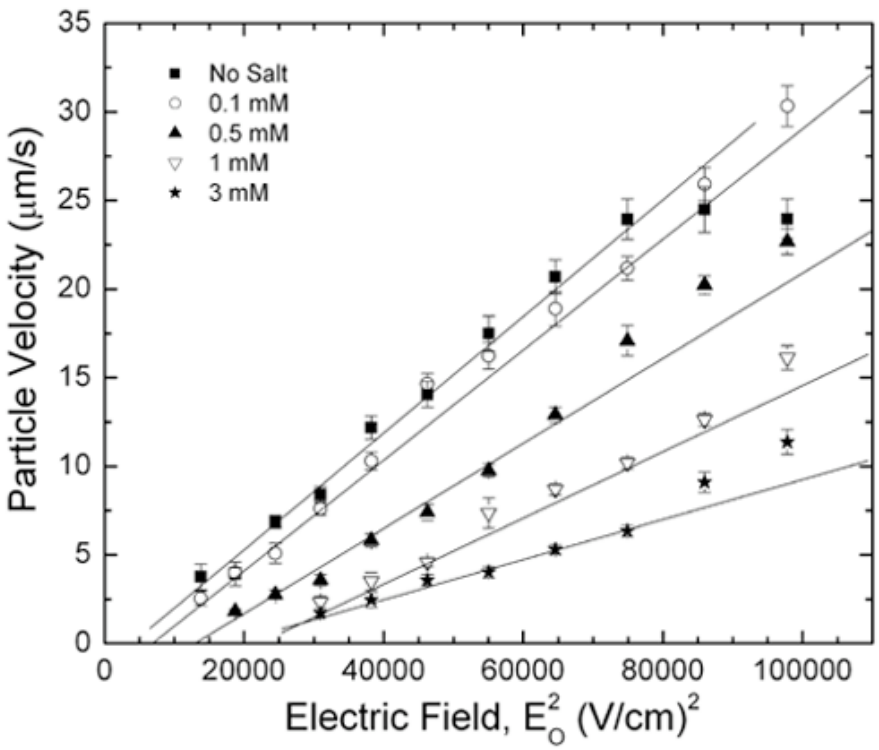
b)

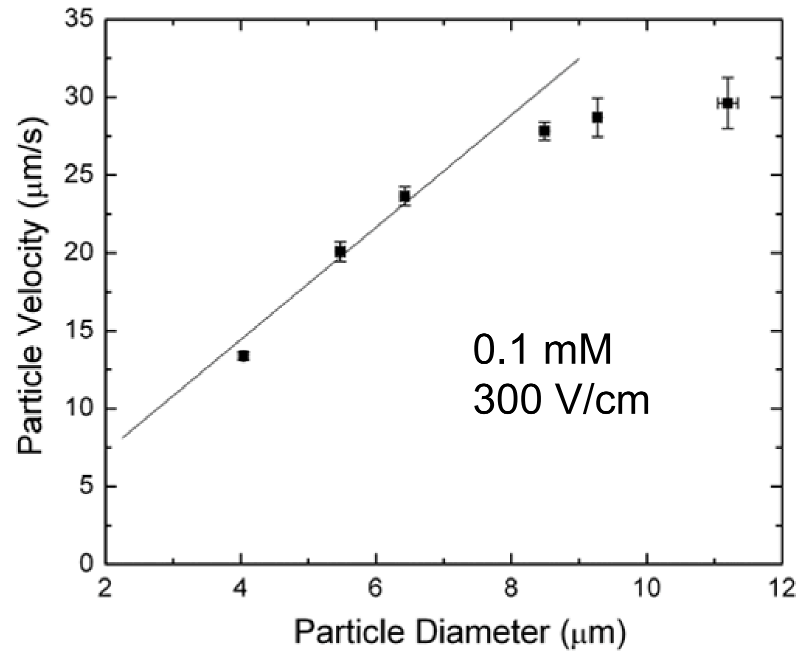






Experimental data



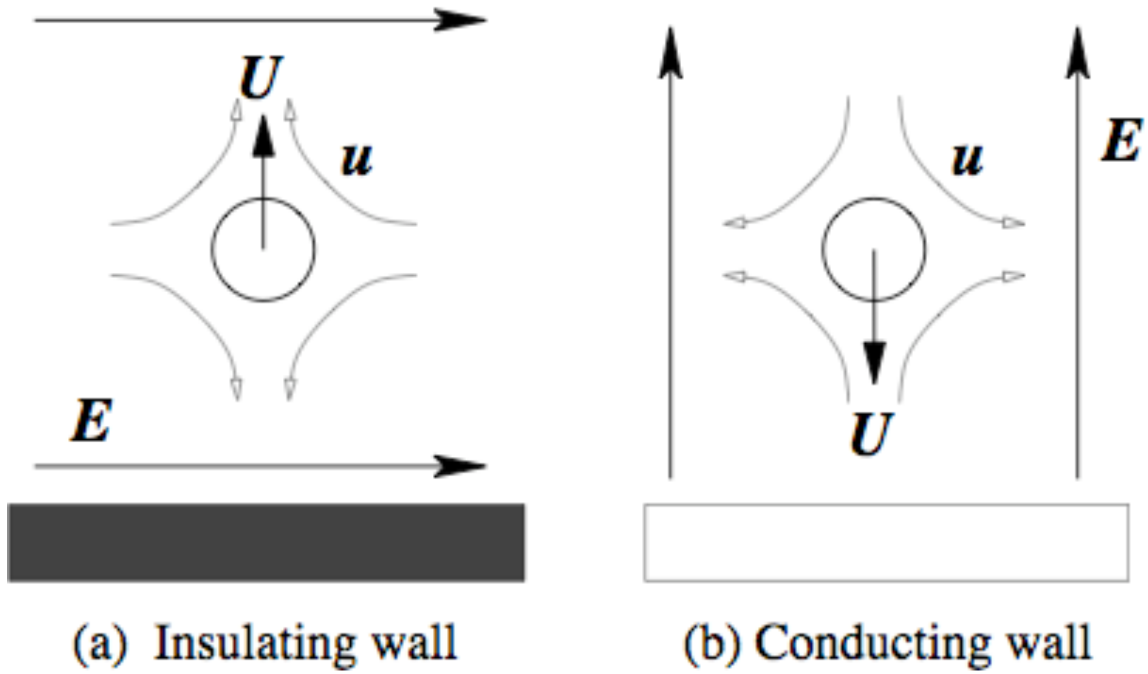


Good fit to theory for

$$c_0 < 1\text{mM},\ ER < 10kT/e,\ \delta = \frac{C_s}{C_D} \approx 10$$

but particles move near the wall… why?

ICEO wall interactions

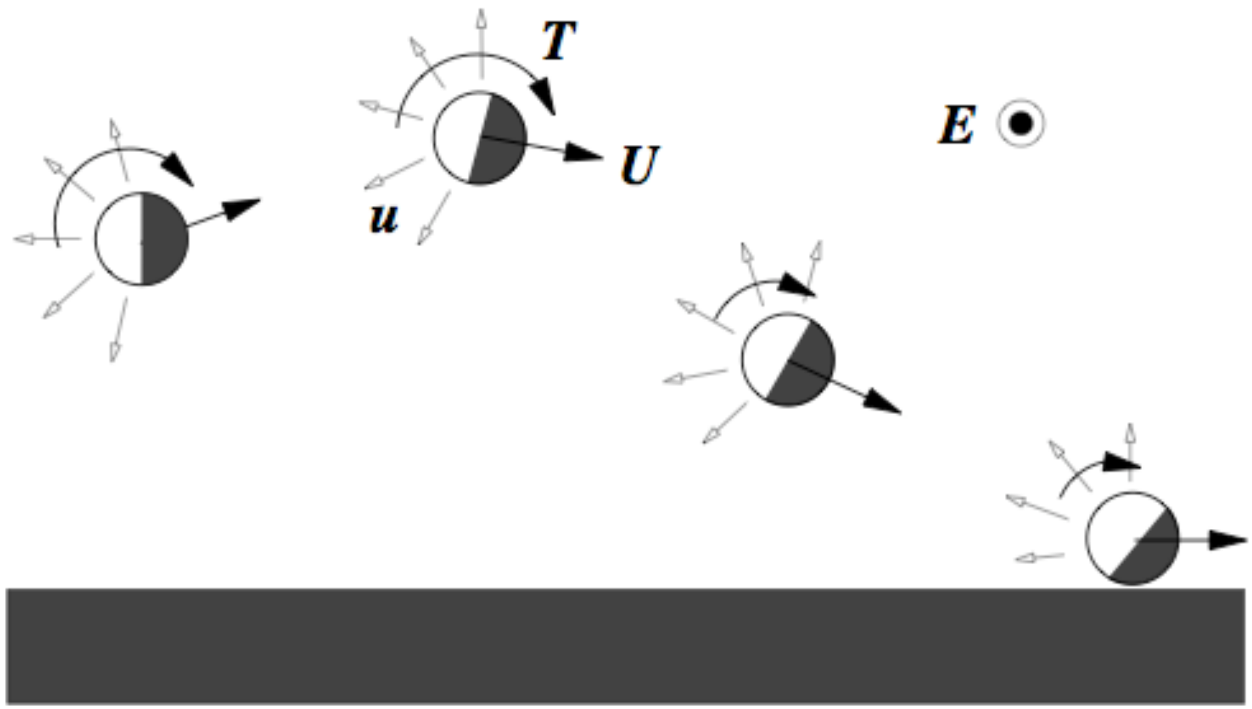


Zhao & Bau, Langmuir (2007)

We expect repulsion from non-polarizable walls, but the Janus particles are attracted to the wall. Why?

ICEP of Janus particles near a wall

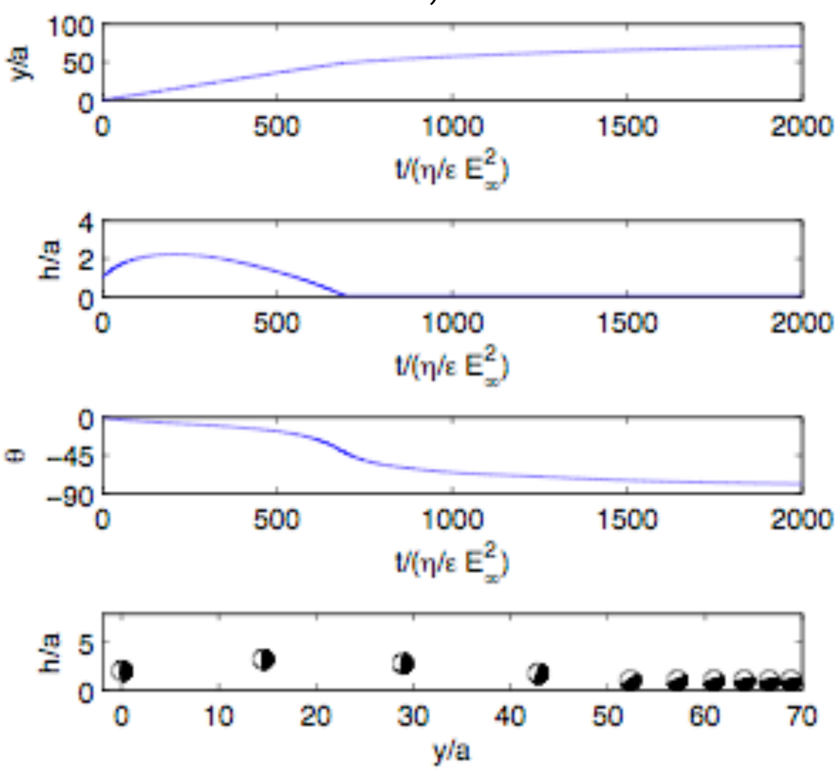
Kilic & Bazant, preprint, arXiv:0712.0453



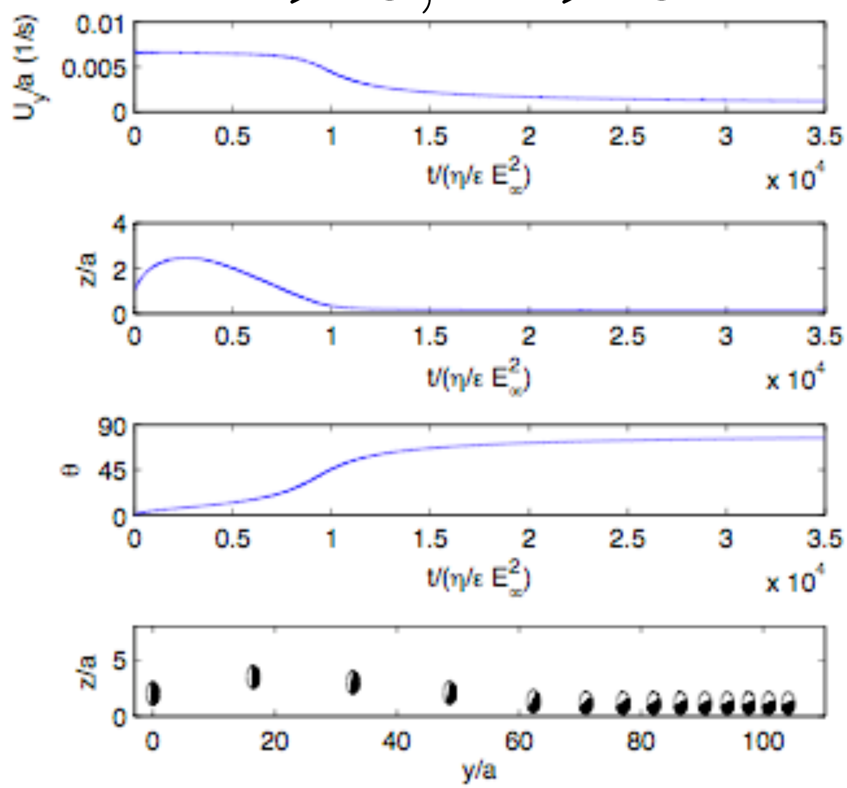
Without tilting, the particle is indeed repelled, but it always rotates to meet the wall and can translate with stable angle.

Simulations of Janus-Wall interaction

$\delta = 0, \ \omega = 0$



$\delta > 5, \ \omega > 5$

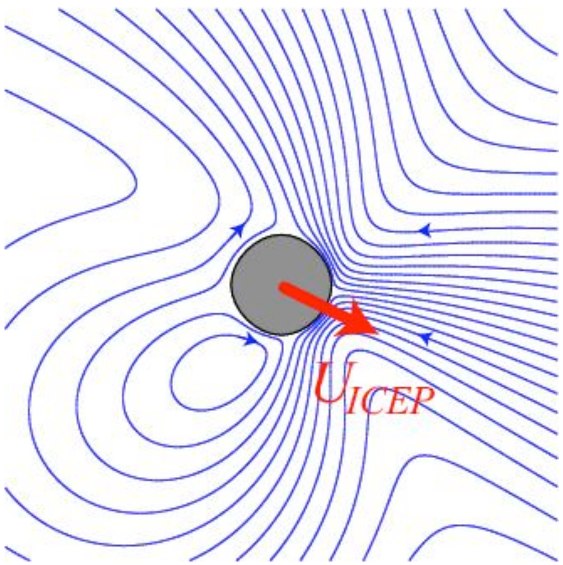


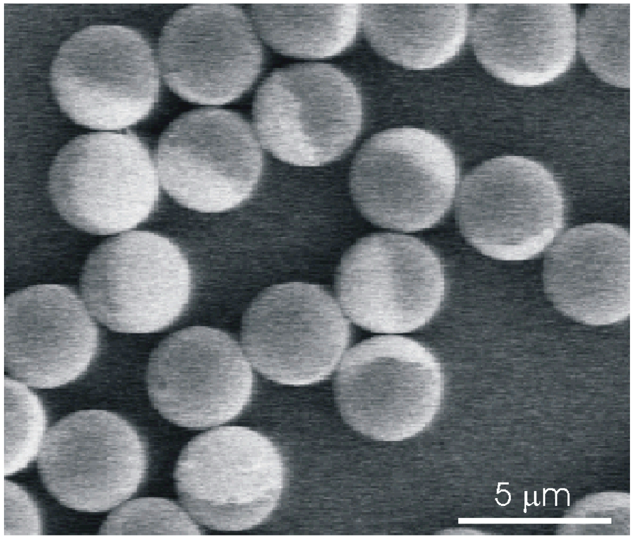
Strong ICEO flows make particle face the wall and get stuck.

Weaker ICEO flows produce tilted translation as observed (due to DEP).

Lecture 3: Conclusion

Nonlinear “induced-charge” electrophoresis leads to many new phenomena in colloids with applications to separation, manipulation, self-assembly. Open questions remain.





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