11/29/04

Today (this week): Electrophoresis
=> "Capstone" Case Study
(A) Experimental methods
(B) Evolution of Analytical Models
(C) "Levich" Models & Results

Next week: "DLVO" Theory & Experiments:
- protein-protein
- receptor-ligand
- cell matrix
- DNA-intranucleus

} interaction

(A) Experimental Methods - see handouts

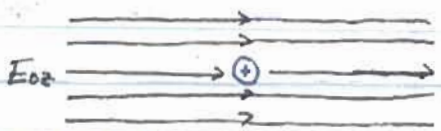
(B) Modeling Approaches ("Free" Elec.)
(1) "qE" vs. "Stoke's Drag" (1800-2004)

$$qE = 6\pi R U \mu \Rightarrow \left(\frac{U}{E_0}\right) \doteq \frac{q}{6\pi R \mu}$$

"electrophoretic mobility"

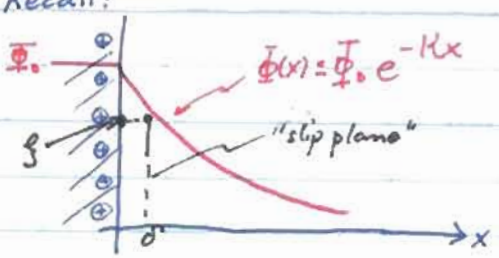
(2) Smoluchowski (1921)
(3) Hückel (1923/4)
(4) Henry (1931)
(5) Levich (1950's, 60's): Analytical model → Experiments.

(B-1) "point charge model"



No disruption of fields, due to continuum approximation

Recall:



at wall, $\sigma_d = \varepsilon\left(-\frac{d\Phi}{dx}\right)\Big|_{x=0}$

"B.C." $\sigma_d = \frac{\varepsilon}{(1/\kappa)}\Phi_0$

$$\sigma_m^{eff} = \frac{\varepsilon}{(1/\kappa)}\zeta$$

Now: $\left(\frac{U}{E_0}\right) = \frac{6_m 4\pi R^2}{6\pi R \mu} = \underbrace{\frac{2}{3}\left(\frac{\varepsilon \zeta}{\mu}\right)\left[\frac{R}{(1/\kappa)}\right]}_{\text{from point charge model}}$

In biology. $1/\kappa \sim 1\,nm$; $R_{cell,\,macromol} \gtrsim 10\,nm$

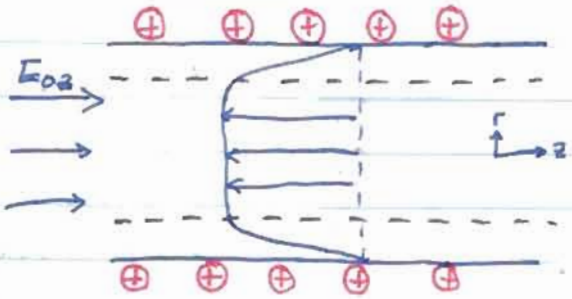
It turns out, this model overestimates U/E_0 by ~10,000.

In reality, there are counter-ions surrounding the charge → E_{0z} acts on both charges → viscous drag; counter-ion retardation

Also, electric field is perturbed due to presence of counter-ions. Convection is perturbed around the finite size particle. Surface conductivity is also ignored.

Phenomena	"Point charge"	Smolechowski (1921)	Hückel	Henry	Levich
① Convective Redistribution of counter-ions ("counter-ion retardation")	No	Yes	Yes	Not really	Yes
② Particle perturbs E-field nearby	No	No	No	"tried"	Yes
③ Self-consistent solution of fluid mechanics	No	No	"tried"	"tried"	Yes
④ Include conductivity of particle & double layer (Surface conductivity)	No	No	No	No	Yes

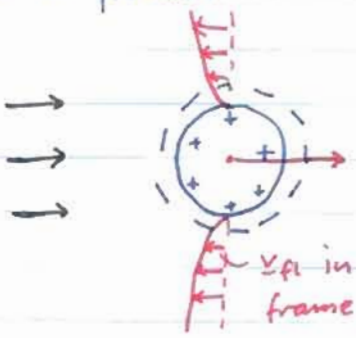
(B-2) Smoluchowski: Assumed $(R \gg 1/\kappa)$



Patterned conceptual "leap" after electroosmosis

$$v_z(r) = -\frac{\varepsilon}{\mu}(\zeta - \Phi(r)) \quad \text{(known)}$$

Change in frames:



same as long as $R \gg 1/\kappa$

$$U = \left(\frac{\varepsilon\zeta}{\mu}\right) E_{0z}$$

But no E-field, convective fluid profile perturbation ...

(B-3) Hückel

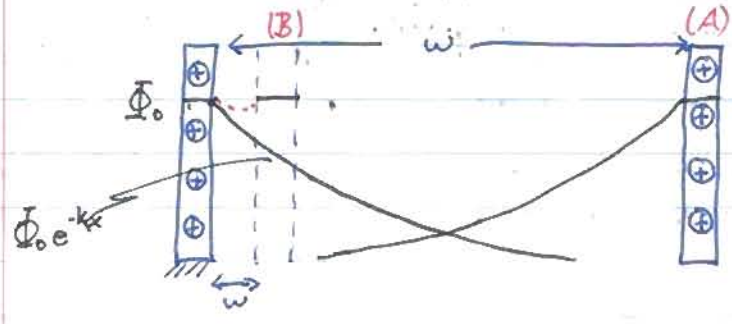
due to fluid mechanics

$$\frac{U}{E} = \left(\frac{2}{3}\right)\frac{\varepsilon\zeta}{\mu}$$

continued on Wednesday

Note on midterm:

highly charged pore walls...



0.1 M NaCl, KCl $\Big\}$ $\frac{1}{\kappa} \sim 1\,nm$

(A) $w \gg 1/\kappa$

↓

eg. 10 nm vs. 1 nm

(B) $w \sim 1/\kappa = 1\,nm$