Electroosmosis (EO) and Electrophoresis (EP)

- A Review of Classical Theories -

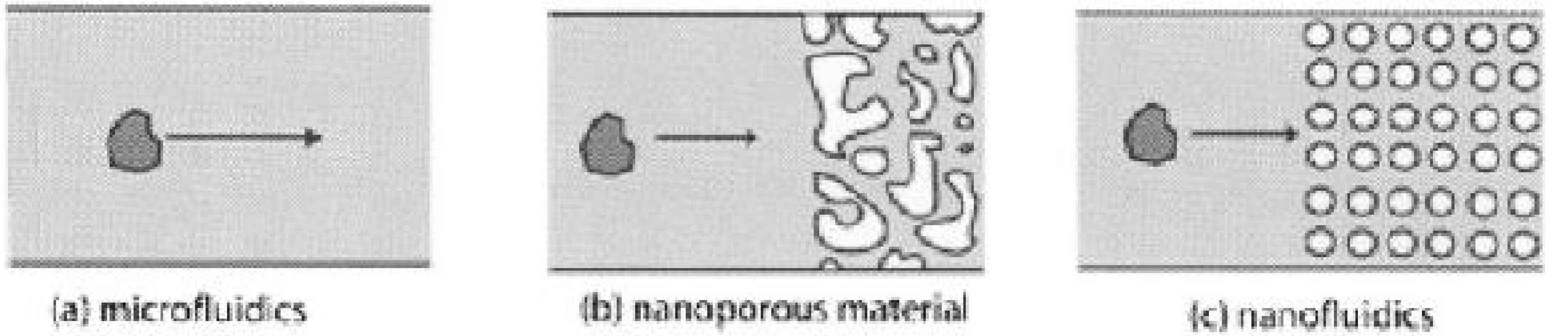
Contents:

April 3, 2008

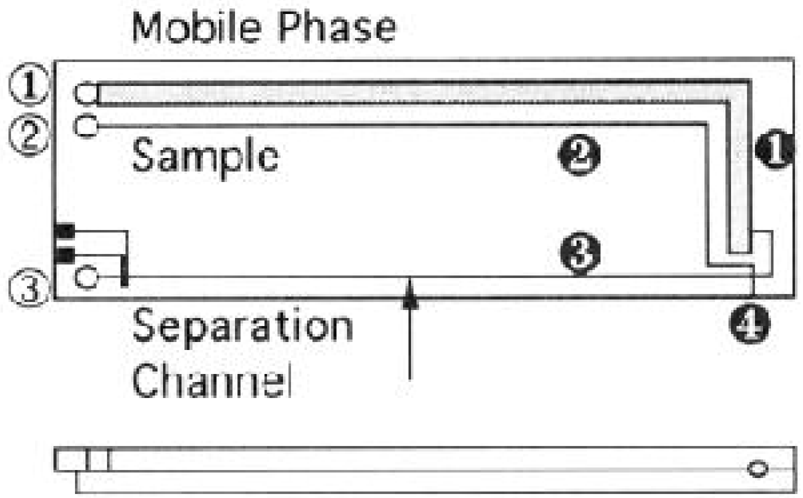
Kengo Ichiki (UofA, NINT)

1. EO/EP & micro/nanofluidics

Micro/nanofluidic devices



[Han (2004) in "Intro. Nanoscale Sci. Tech.]

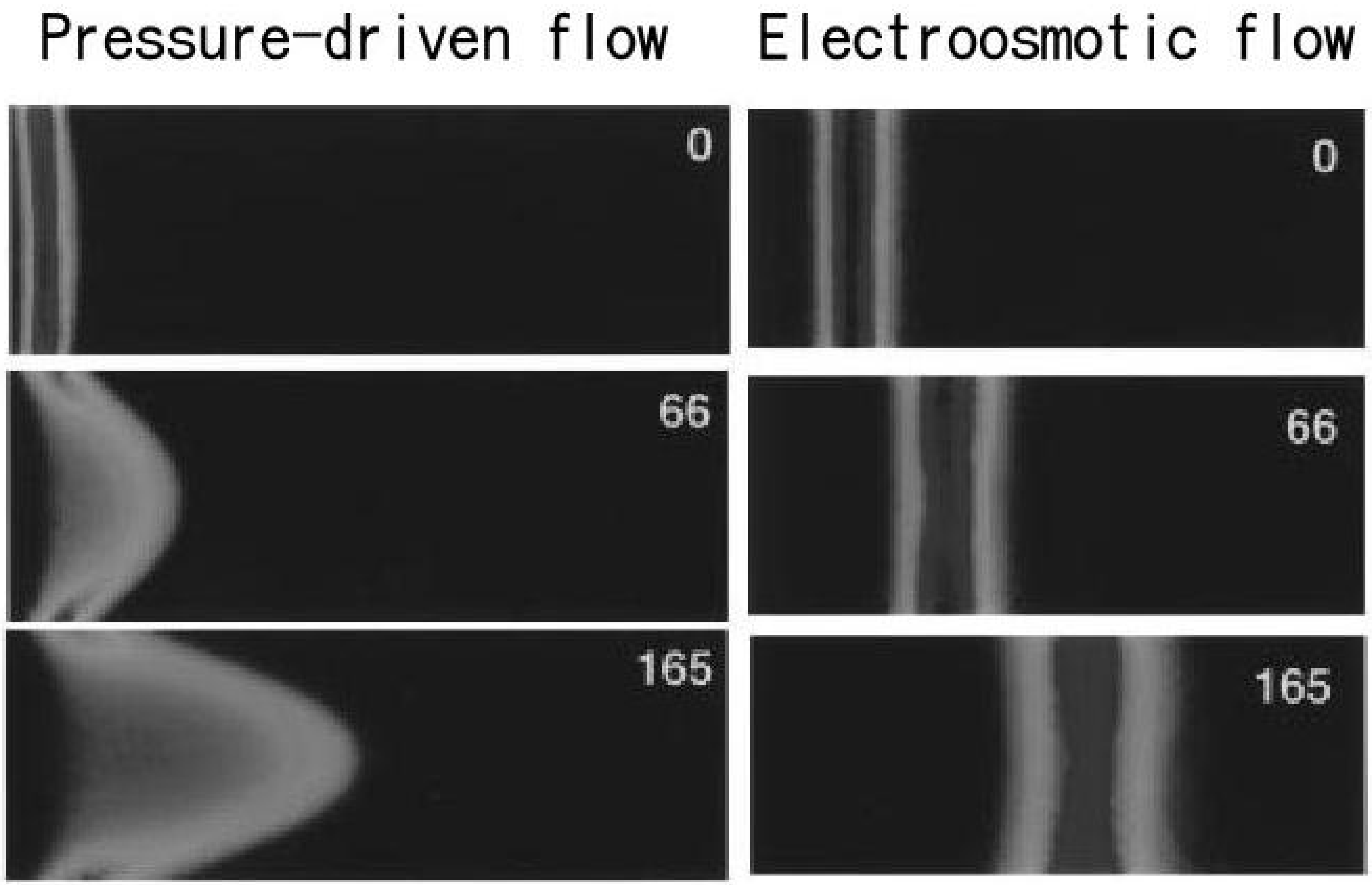


[Harrison et al (1992) Anal.Chem.64, 1928-1932]

How to pump?

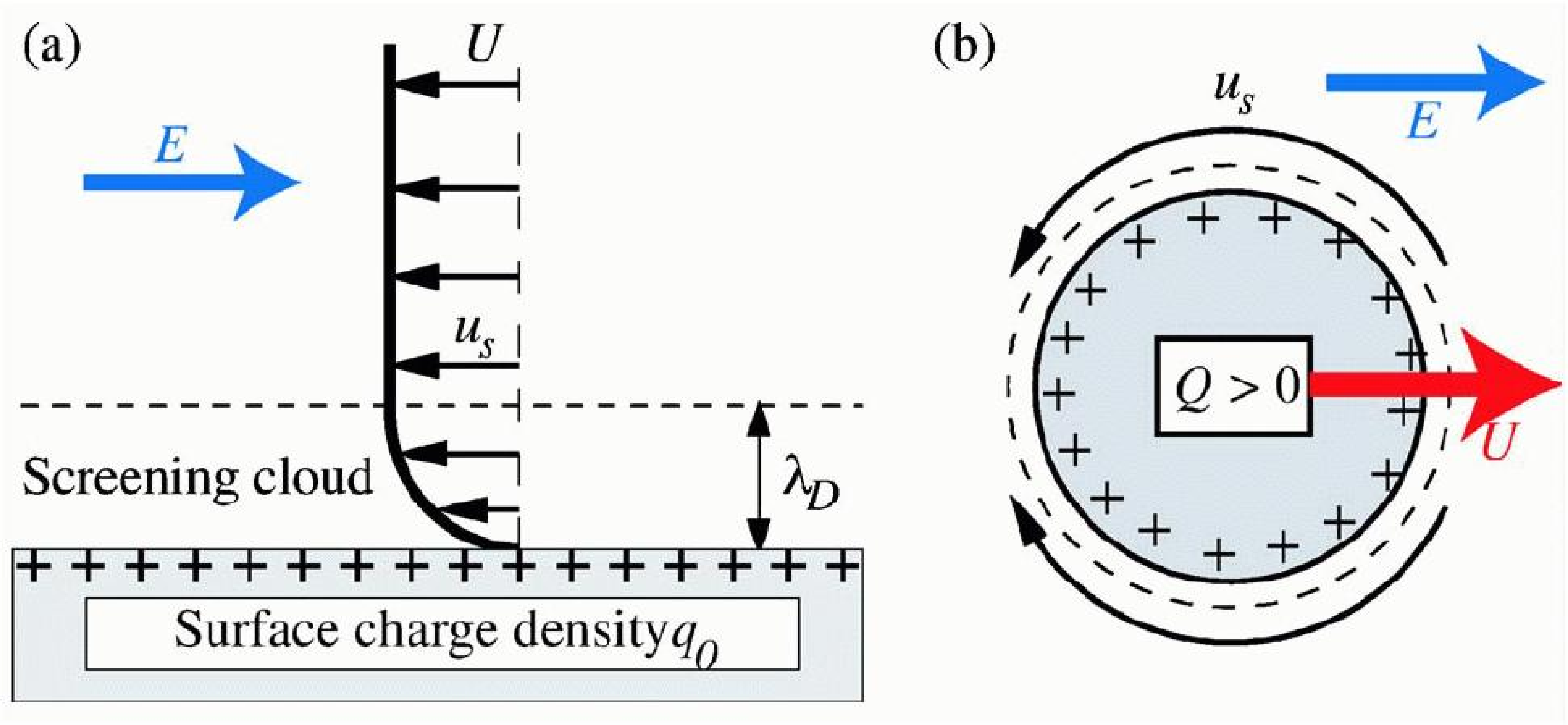
- by pressure
- by electric field

1. EO/EP & micro/nanofluidics



[Paul, Garguilo, Rakestraw (1998) Anal.Chem.70, 2459-2467]

2. Phenomena - EO/EP



[Squires, Quake (2005) Rev.Mod.Phys.77, 977-1026]

3. Basic Theory

Three fields:

- fluid velocity (Stokes eq.)
  - $\mathbf{0} = -\boldsymbol{\nabla} p + \mu \nabla^2 \boldsymbol{u} - \rho_e \boldsymbol{\nabla} \phi$
  - $\boldsymbol{\nabla} \cdot \boldsymbol{u} = 0$
- electric field (Poisson eq.)
  - $\nabla^2 \phi = -\dfrac{\rho_e}{\epsilon \epsilon_0}$
- ion density (Nernst-Planck eq.)
  - $\dfrac{\partial n_i}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{J}_i$
  - $\boldsymbol{J}_i = n_i \boldsymbol{v}_i = -D_i \left(\boldsymbol{\nabla} n_i + \dfrac{z_i e n_i}{kT} \boldsymbol{\nabla} \phi \right) + n_i \boldsymbol{u}$
  - $\rho_e = \sum_i z_i e n_i$

3. Basic Theory - Approximations

Boltzmann distribution

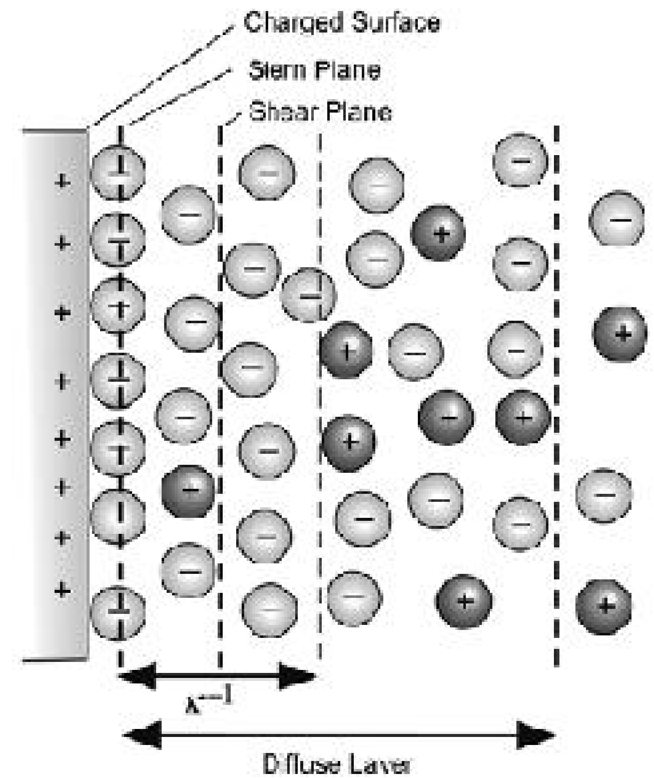
- $n_i(\boldsymbol{x}) = n_i^\infty \exp\left(-\frac{z_i e \phi(\boldsymbol{x})}{kT}\right)$ (Note: $\boldsymbol{J} = \boldsymbol{0}$ for $\boldsymbol{u} = \boldsymbol{0}$.)

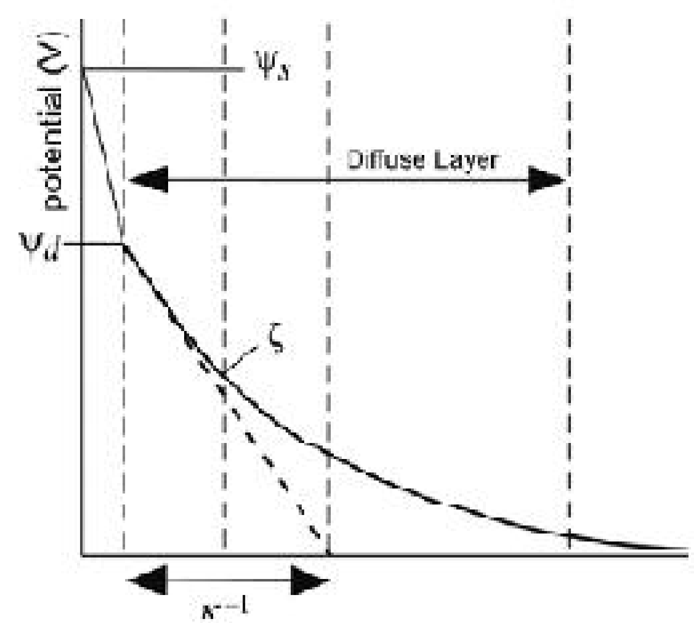
In this case, Poisson-Boltzmann eq.

- $\nabla^2 \phi = -\sum_i \frac{z_i e n_i^\infty}{\epsilon \epsilon_0} \exp\left(-\frac{z_i e \phi}{kT}\right)$

Debye-Huckel approximation (linearized PB eq.)

- $\nabla^2 \phi = \kappa^2 \phi, \quad \text{where} \quad \kappa^2 = \sum_i \frac{(z_i e)^2 n_i^\infty}{\epsilon \epsilon_0 kT}$

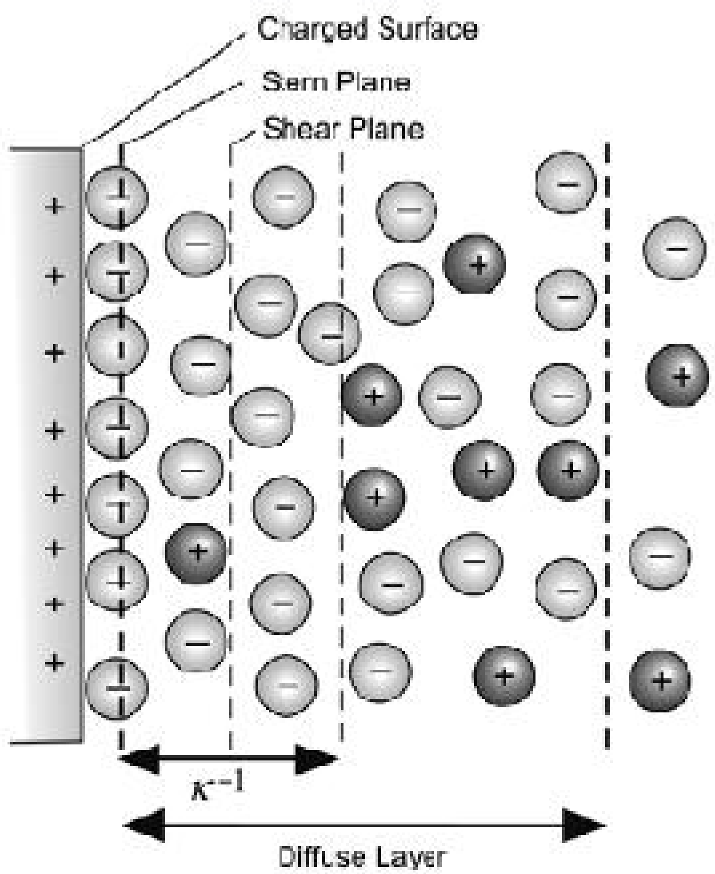


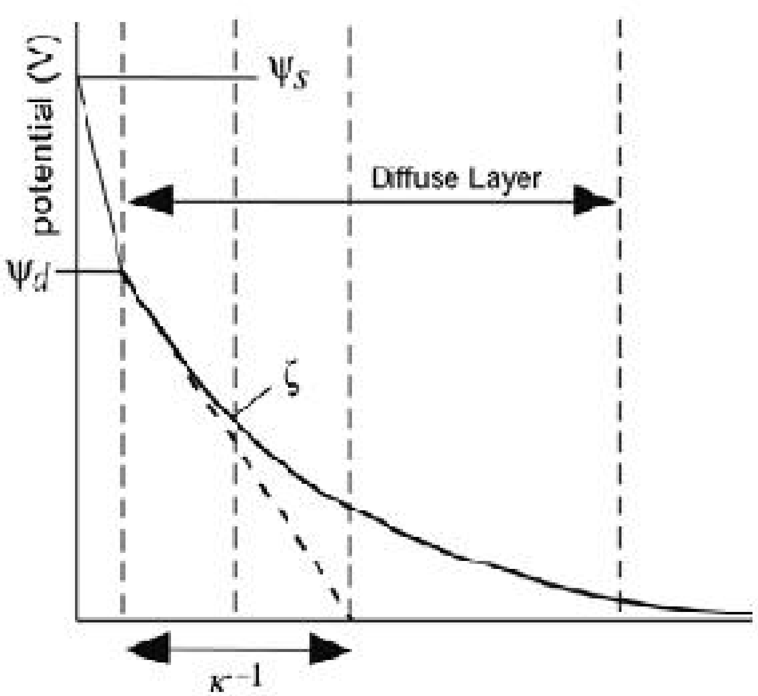


- Solutions:
  - $\phi = \phi_s e^{-\kappa z}$ for plane
  - $\phi = \phi_s \frac{a}{r} e^{-\kappa(r-a)}$ for sphere

[Masliyah, Bhattacharjee (2006)]

3. Basic Theory - Zeta Potential





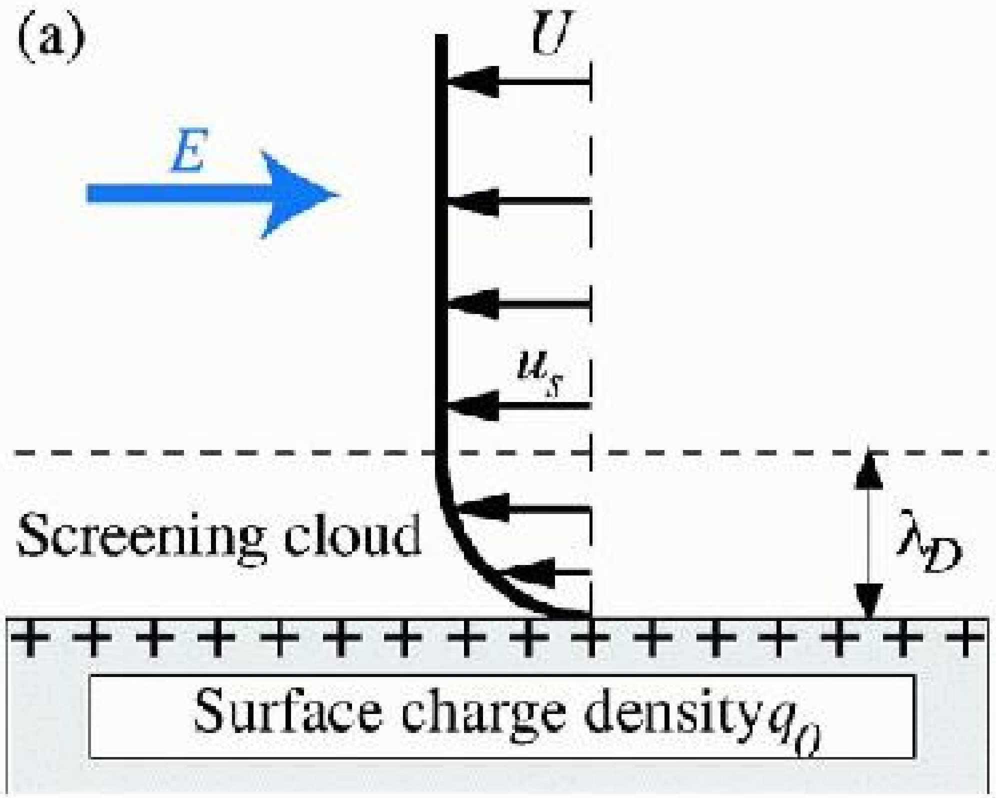
[Masliyah, Bhattacharjee (2006)]

- Problem - finite size of ions
  - $n_i(\boldsymbol{x}) = n_i^\infty \exp\left(-\frac{z_i e \phi(\boldsymbol{x})}{kT}\right)$
  - $\phi = \phi_s e^{-\kappa z}$ for plane
- Stern layer
  - where immobile ions are stuck at the surface
- Zeta potential
  - the potential at which the no-slip B.C. is applied
  - (= shear plane)
  - $\zeta \approx \phi_{\text{Stern}}$ (conventionally)
- Note: zeta potential is
  - a general (phenomenological) parameter
  - characterizing the surface properties
  - both physically and chemically

3. Basic Theory - Electroosmosis

Helmholtz-Smoluchowski formula

- $\boldsymbol{u}_s = -\frac{\epsilon\epsilon_0\zeta}{\mu}\boldsymbol{E}_\parallel$



[Squires, Quake (2005) Rev.Mod.Phys.77, 977-1026]

- obtained from the Stokes eq.

$$0 = \mu\frac{\mathrm{d}^2 u_x}{\mathrm{d}z^2} - \epsilon\epsilon_0\frac{\mathrm{d}^2\phi}{\mathrm{d}z^2}E_x$$

- Assumptions:
  - Debye-Huckel approximation

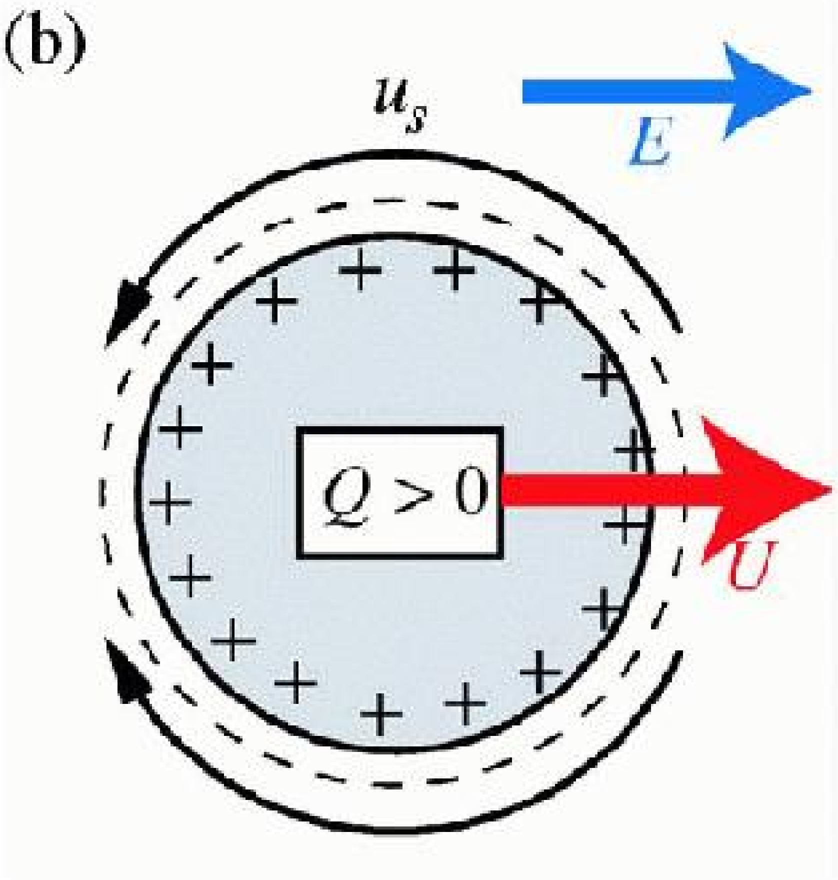
    $\phi = \zeta e^{-\kappa z}$
  - thin double layer

    $\kappa a \gg 1$

3. Basic Theory - Electrophoresis

Smoluchowski formula

- $$\boldsymbol{U} = \frac{\epsilon\epsilon_0\zeta}{\mu}\boldsymbol{E}_\infty$$



[Squires, Quake (2005) Rev.Mod.Phys.77, 977-1026]

- obtained from the slip B.C.

$$\boldsymbol{u}_s = -\frac{\epsilon\epsilon_0\zeta}{\mu}\boldsymbol{E}_\parallel$$

- => the same assumptions:
  - Debye-Huckel approximation
  - thin double layer

- Note: Morrison (1970) showed
  - it is valid for arbitrary shaped objects!

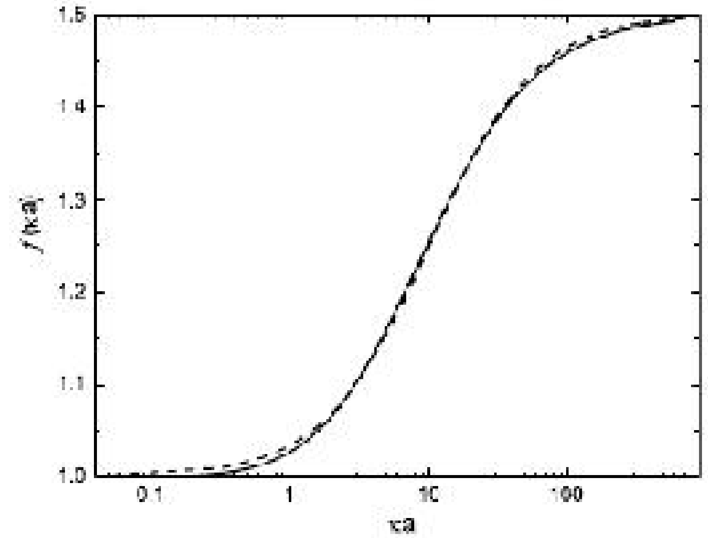
4. Extensions

- thickness of double layer
  - Henry (1930)
- boundary conditions (constant charge)
  - Teubner (1982)
  - Anderson (1985)
- shape of the particle
  - Morrison (1970)
- distortion of double layer
  - Dukhin, Derjaguin (1974) theory for thin DL
  - O'Brien, White (1978) numerical for arbitrary DL
  - O'Brien (1983) theory for thin DL
- polarization of the particles
  - Bazant, Squires (2004), Squires, Bazant (2004, 2006)

4. thickness of double layer

Thick double layer limit (Huckel limit) $\kappa a \ll 1$

- $$\boldsymbol{U} = \frac{2}{3}\frac{\epsilon\epsilon_0\zeta}{\mu}\boldsymbol{E}_\infty$$



[Masliyah, Bhattacharjee (2006)]

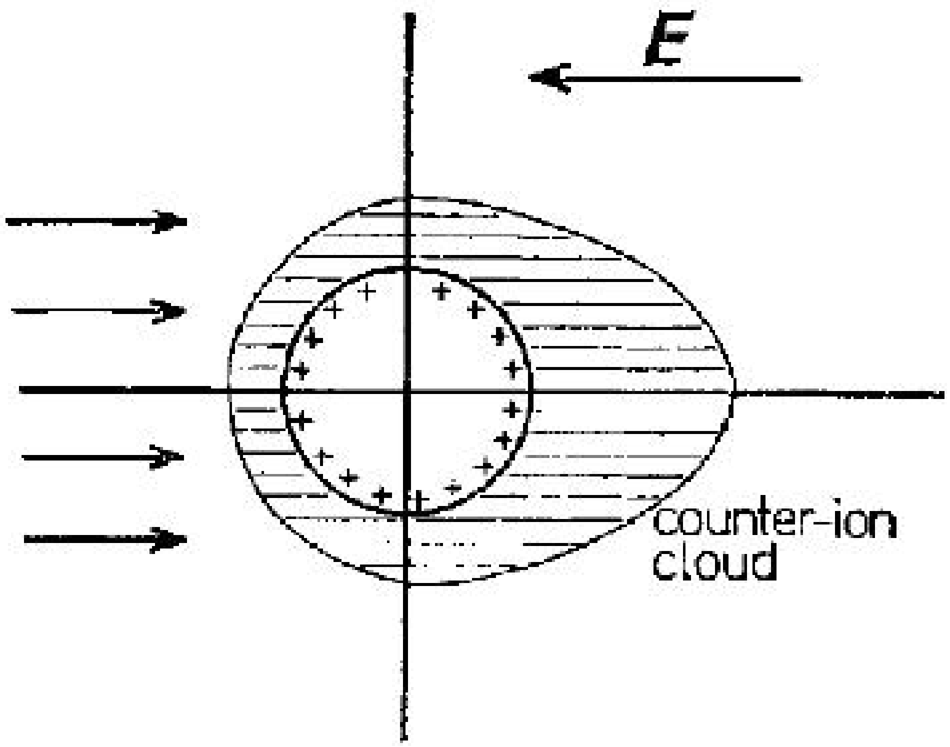
For arbitrary thickness (Henry 1930)

$$\boldsymbol{U} = \frac{\epsilon\epsilon_0\zeta}{\mu}\boldsymbol{E}_\infty f(\kappa a)$$

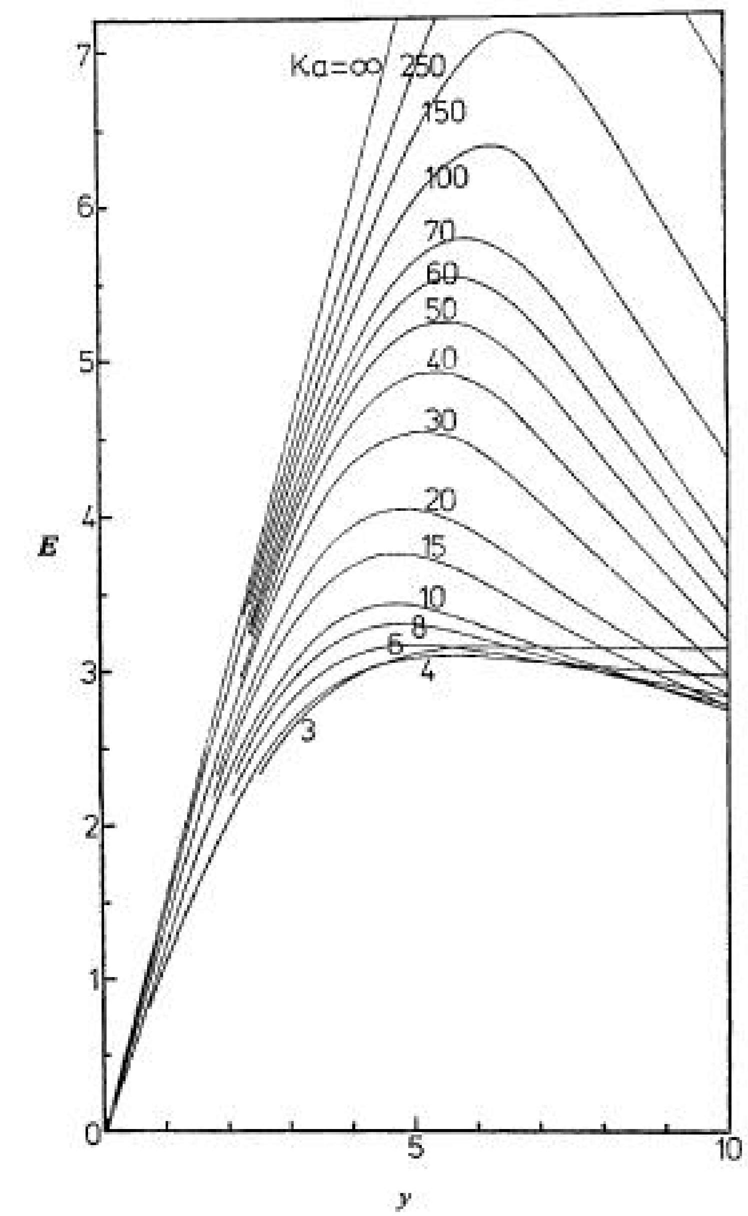
- $$= \frac{\epsilon\epsilon_0\zeta}{\mu}\boldsymbol{E}_\infty \frac{2}{3}\left(1 + \frac{(\kappa a)^2}{16} - \frac{5(\kappa a)^3}{48} - \frac{(\kappa a)^4}{96} + \frac{(\kappa a)^5}{96} - \frac{(\kappa a)^6 - 12(\kappa a)^4}{96} e^{\kappa a}\int_{\kappa a}^{\infty}\frac{e^{-t}}{t}\mathrm{d}t\right)$$

4. distortion of double layer

so called "polarization effect of DL"



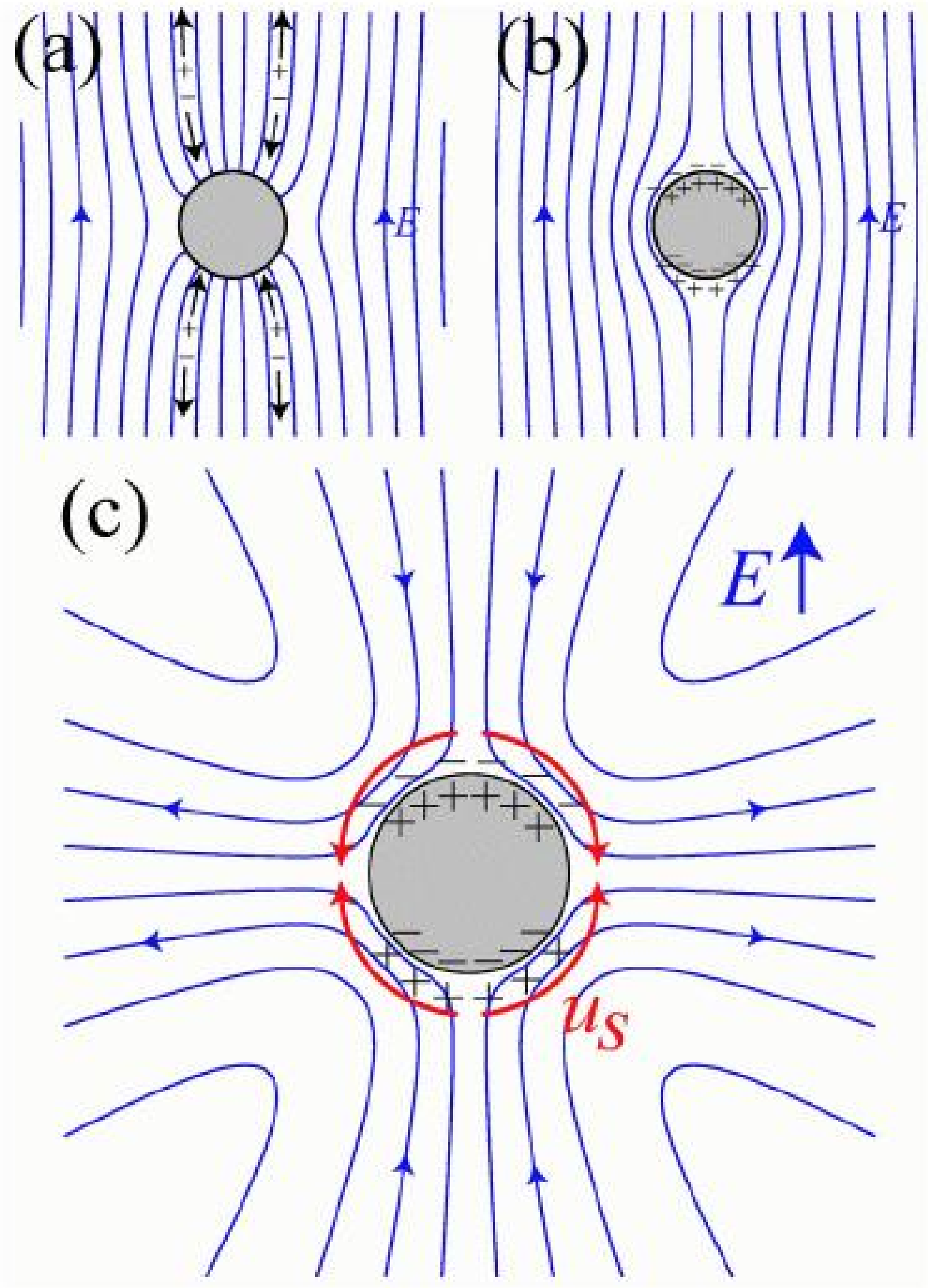
[O'Brien, White (1978) J.Chem.Soc.Faraday Trans.2 74, 1607-1626]



4. polarization of particles

for conducting particle

- "induced-charge EO"
- "induced-charge EP"

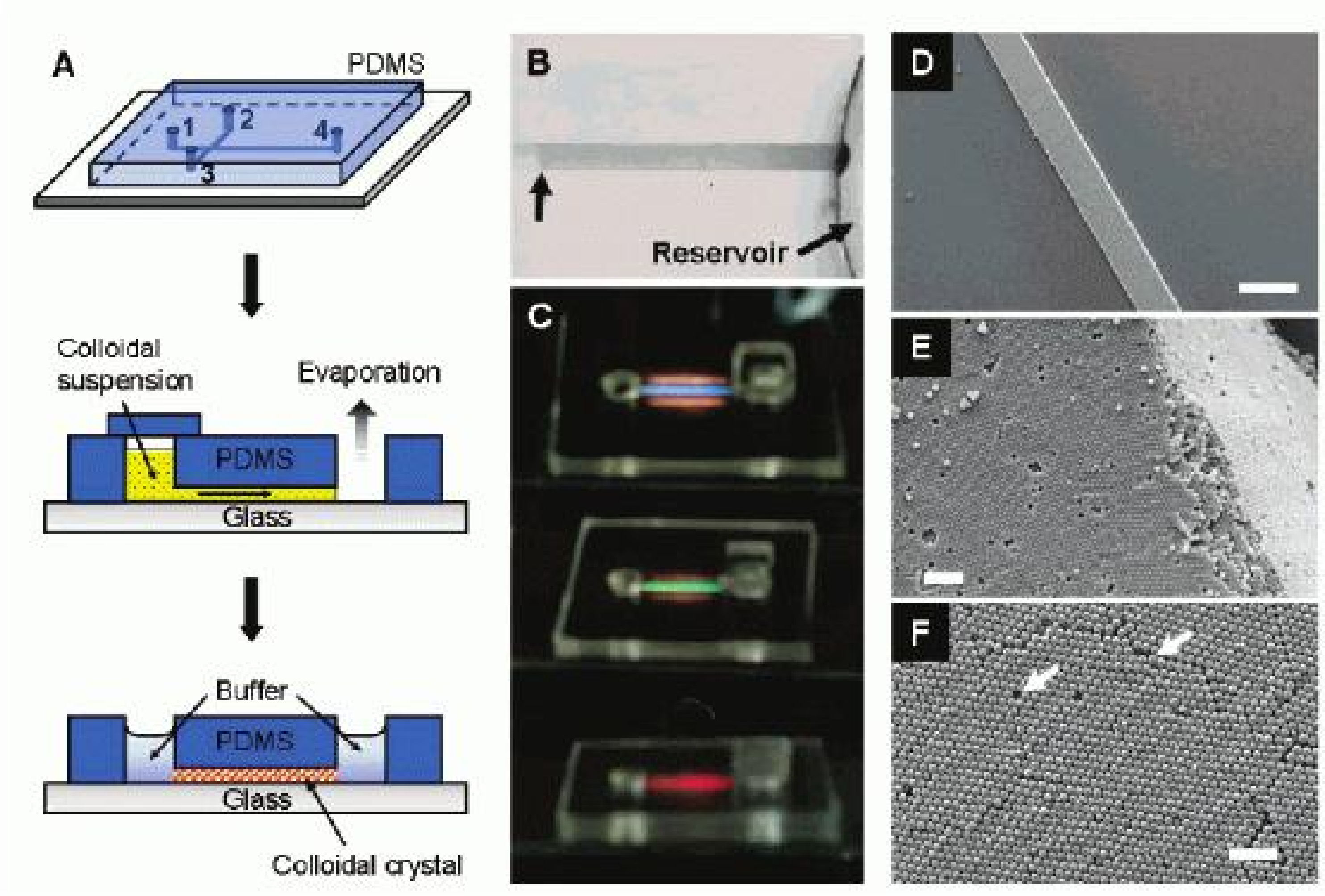


[Squires, Quake (2005) Rev.Mod.Phys.77, 977-1026]
[Bazant, Squires (2004), Squires, Bazant (2004, 2006)]

5. Discussions

What we want to study?

"NANO-fluidic device!"



[Zeng, Harrison (2007) Anal.Chem.]

5. Discussions (continued)

Multi-Scales:

- macro. theory (here)
- molecular theory!

Similar phenomena:

- thermophoresis
- electro-acoustics
- electro-magneto-phoresis

References

Han (2004) in "Intro. Nanoscale Sci. Tech."

Paul, Garguilo, Rakestraw (1998) Anal.Chem.70, 2459-2467

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