Transport and Electrokinetics in Nanoscale Fluids

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Course Website: **nanoHUB.org**
Compass.illinois.edu

Back to Constitutive Equations

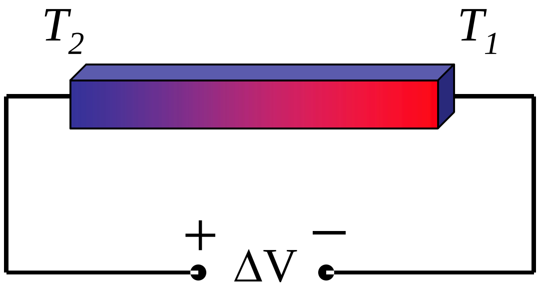
- Hooke's Law $\sigma = E\varepsilon$
- Fourier's Law $\mathbf{q} = -k\nabla T$
- Fick's Law of Diffusion $\mathbf{J} = -D\nabla C$
- Newton's law on shear stress $\tau = -\mu\,(du/dy)$
- Ohm's Law $J = \sigma E$

How are they correlated in the nanoscale?

Coupled Heat and Electron Conduction

- Seebeck effect (1821)

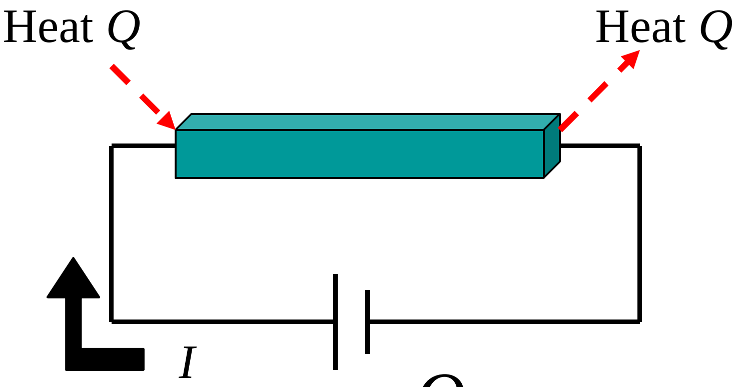
(Heat to electricity)



$$S = -\frac{\Delta V}{T_2 - T_1} \quad [\text{V/°K}]$$

- Peltier effect (1834)

(Electric cooling)



$$\pi = \frac{Q}{I}$$

Principle of Thermoelectric Effect

Electron Current by BTE:

$$\mathbf{J}_e = \sigma_e \mathbf{E} + \frac{k_B \sigma_e}{e} \nabla \left(T_e \ln n_e \right)$$

Thermoelectricity:

$$\mathbf{E} = \frac{k_B}{e} \nabla \left(T_e \ln n_e \right)$$

Seebeck coefficient:

$$S = \frac{\partial \mathbf{E}}{\partial T} = -\frac{k_B}{e} \boxed{\left(\ln n_0 + \frac{E_a}{k_B T} \right)}$$

86μV/K

- **Density of electrons (n)**
- **Activation energy (Ea)**

Thermoelectric Figure of Merit

Electronic current

$$\mathbf{J}_e = \sigma_e(\mathbf{E} + S\nabla T)$$

Thermal current

$$\mathbf{J}_Q = \kappa\nabla T - \pi\sigma\mathbf{E} = \kappa\nabla T - (ST)\sigma\mathbf{E}$$

Seebeck Coefficient

Conductivity

Temperature

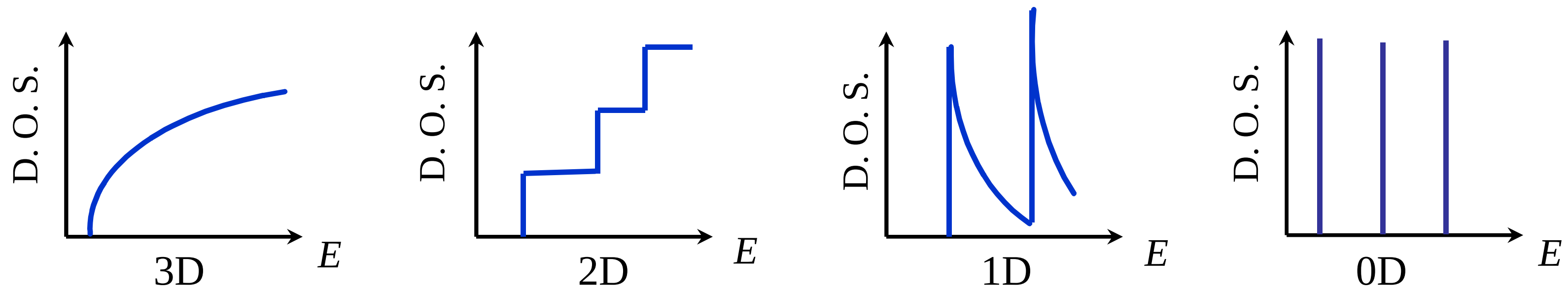
Figure of Merit

$$ZT = \frac{S^2\sigma T}{\kappa}$$

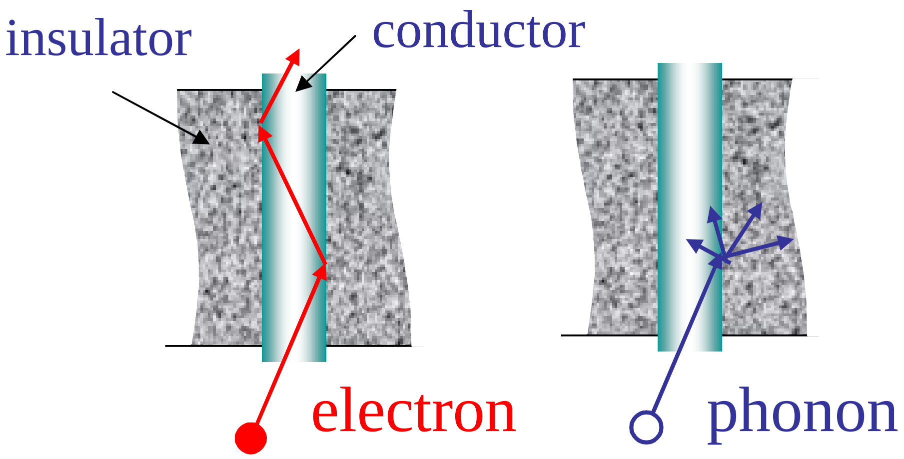
Thermal Conductivity (from electron+phonon)

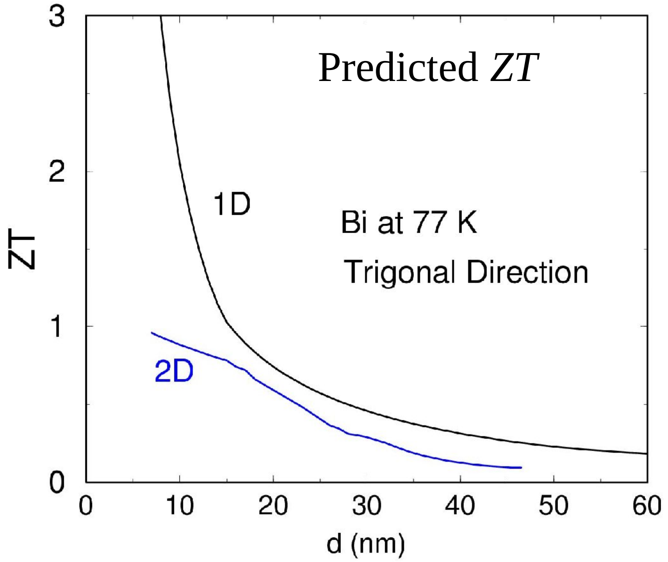
New Directions for Nano- Thermoelectricity

- Electronic properties may be dramatically modified due to the electron confinement in nanostructures which exhibit low-dimensional behaviors

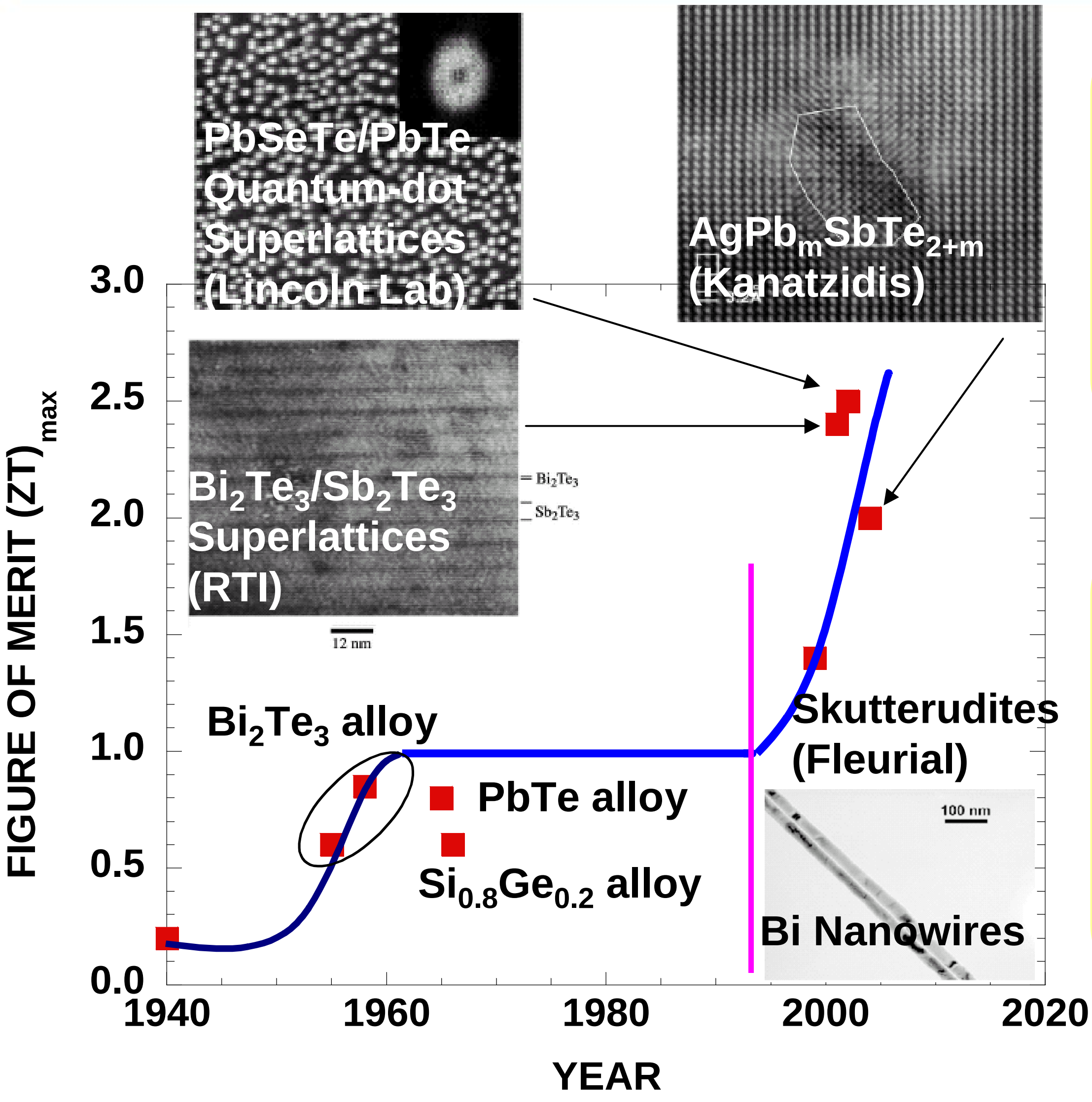


- Thermal conductivity can be significantly reduced by the preferential scattering of phonons at the interfaces





State-of-the-Art in Thermoelectrics



PbTe/PbSeTe	Nano	Bulk
$S^2\sigma$ (μW/cmK^2)	32	28
k (W/mK)	0.6	2.5
ZT (T=300K)	1.6	0.3

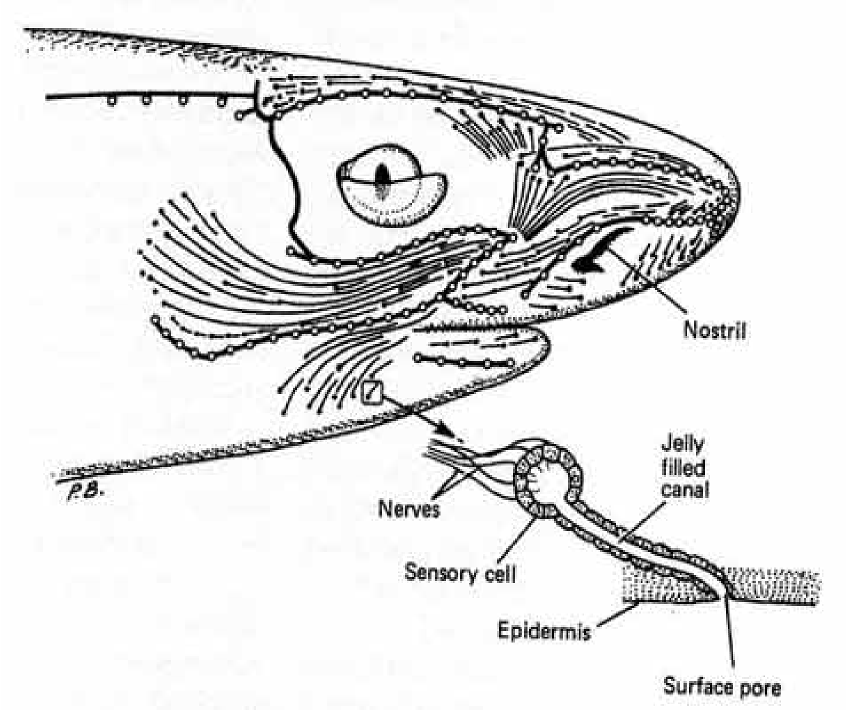
Harman et al., Science (2003)

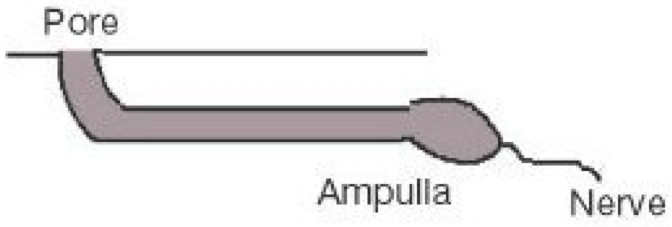
Bi$_2$Te$_3$/Sb$_2$Te$_3$	Nano	Bulk
$S^2\sigma$ (μW/cmK^2)	40	50.9
k (W/mK)	0.6	1.45
ZT (T=300K)	2.4	1.0

Venkatasubramanian et al., Nature, 2002.

A Natural Thermo-electric Sensor in Shark

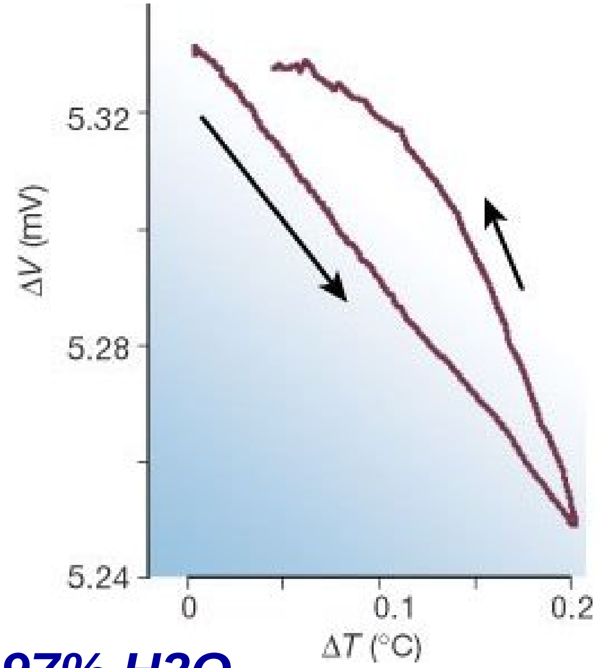
Brown, Nature, 2003





Extreme sensitivity to temperature changes

~0.001°C !!

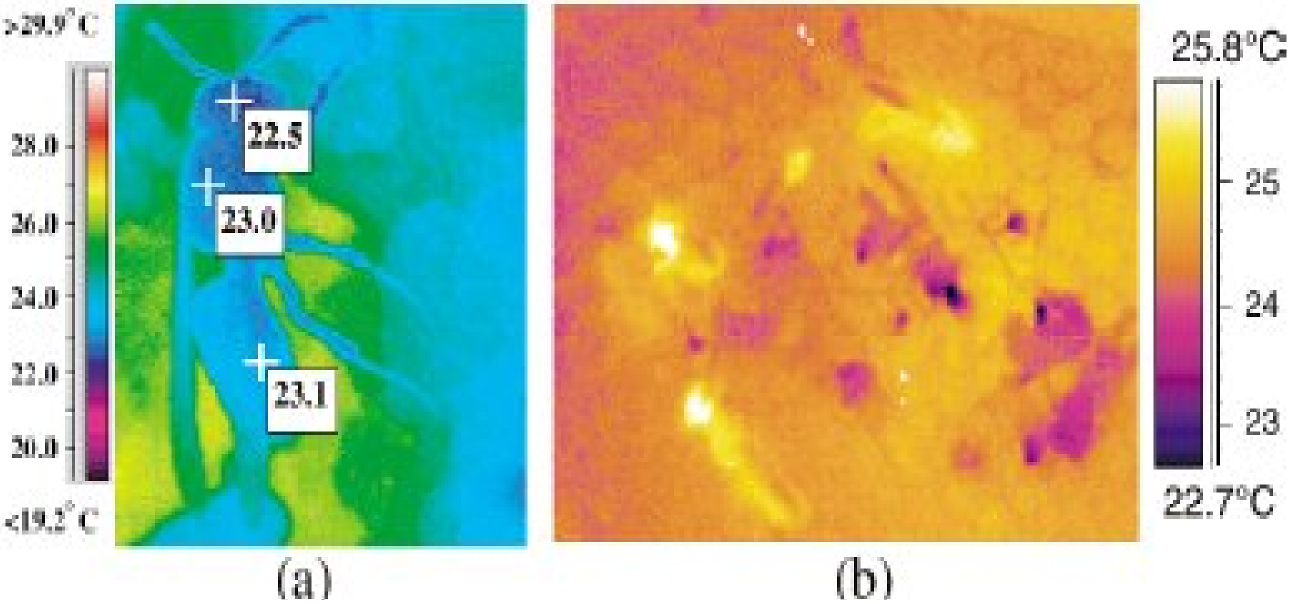


97% H2O

Sulfated glycoprotein

Na, Ca, Cl, and K ions.

Hornet skin: a natural heat pump?



IR image of the hornets

Hornets keep their body temperature lower by 3-4 degrees when they are active outside the nest in daytime, where the ambient temperature can be as high as 40–60 C.

(Ishay et al, PRL, 2003)

Making the Connection

- Coupled transport is not unique to solid
- It applies to liquid and gas systems
- Migration of fluid can be associated with applied electric, thermal or optical fields

Organization of Coming Lectures

- Coupled Charge-Mass Transport in Fluid
  - Electrokinetic Phenomena
- Surface and Interface Interactions
  - Contact Angle
- Friction, Lubrication and Adhesion

Conduction of Ions in Fluids

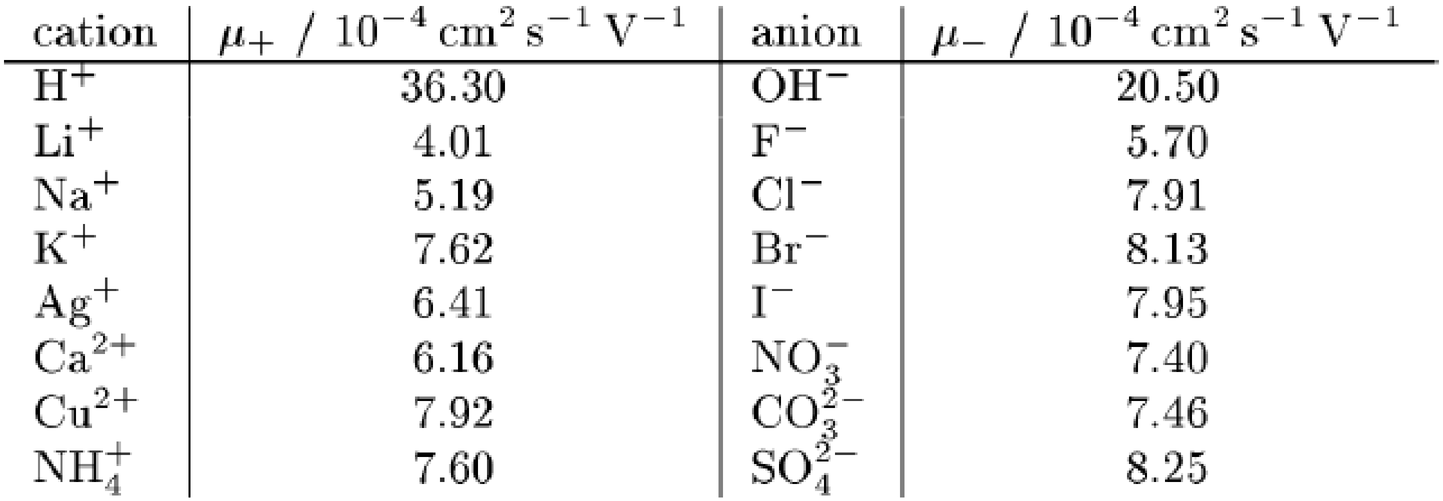
$$J_{ion} = \frac{\partial}{\partial z}\left(eZ\frac{k_B T n_{ion}\langle\tau\rangle}{m_{ion}}\right) + F_z\frac{eZn_{ion}\langle\tau\rangle}{m_{ion}}$$

Mobility:

$$\mu_{ion} = \frac{eZ\langle\tau\rangle}{m_{ion}}$$

Conductivity:

$$\sigma_{ion} = eZ\mu_{ion}n_{ion}$$



cation	μ_+ / $10^{-4}\,\mathrm{cm}^2\,\mathrm{s}^{-1}\,\mathrm{V}^{-1}$	anion	μ_- / $10^{-4}\,\mathrm{cm}^2\,\mathrm{s}^{-1}\,\mathrm{V}^{-1}$
H^+	36.30	OH^-	20.50
Li^+	4.01	F^-	5.70
Na^+	5.19	Cl^-	7.91
K^+	7.62	Br^-	8.13
Ag^+	6.41	I^-	7.95
Ca^{2+}	6.16	NO_3^-	7.40
Cu^{2+}	7.92	CO_3^{2-}	7.46
NH_4^+	7.60	SO_4^{2-}	8.25

Table 2.1. Ionic mobilities μ_i in water solution at $T = 298\,\mathrm{K}$

From: Jens Ducrée, http://www.myfluidix.com/

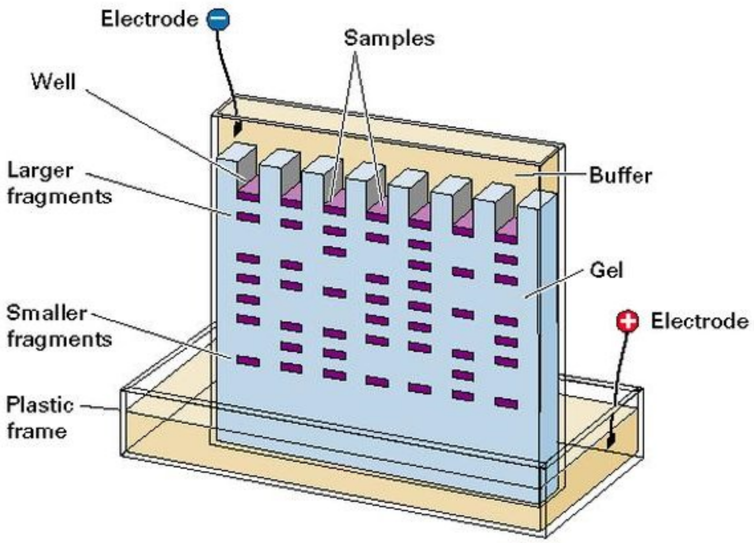
Applications of Ion Migration

Gel Electrophoresis:

- Separation of larger molecules with smaller ones by their mobility in gels

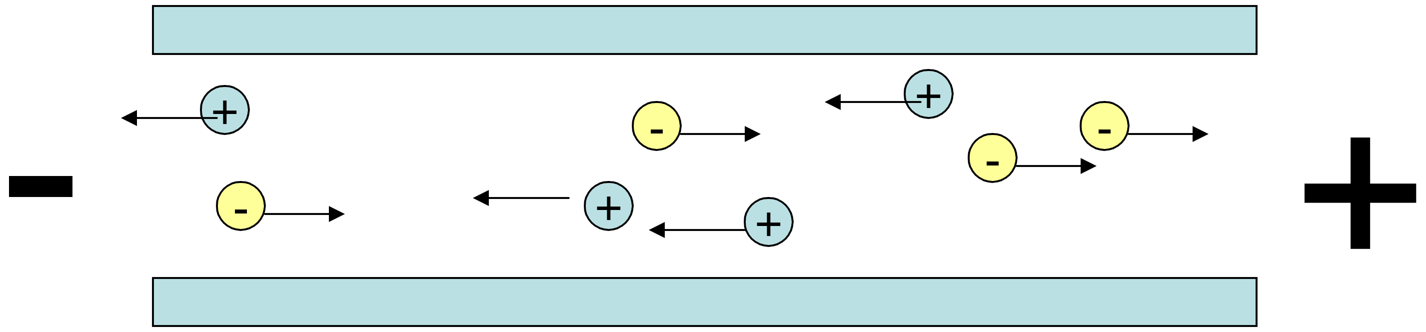
- Competing with diffusion so low diffusivity preferred

- For 15-20 cm long gel, the separation time is about hours



http://www.cbs.dtu.dk/staff/dave/roanoke/genetics980211.html

Electrophoresis



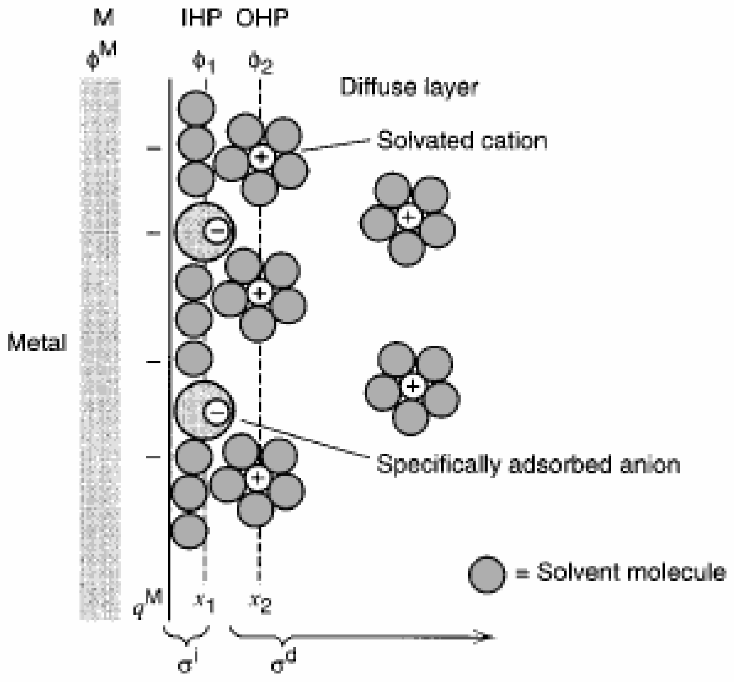
- Ions migrate under E fields
- Friction drag to surrounding molecules (induced flow)
- Joule Heating: increased temperature due to omic effects
- non uniform temperature -> non uniform velocity

Electric Double Layer

Poisson Equation due to space charges

$$\nabla^2 U(\vec{r}) = \sum \frac{e}{\varepsilon} Z_{ion} c_{ion}(\vec{r})$$

$$\sum e Z_{ion} c_{ion}(\vec{r}) = eZ(n_+ - n_-)$$



Presence of space charges due to thermal excitation:

$$c_{ion} = c_0 \exp(-eZ_{ion} U(\vec{r})/k_B T)$$

Debye Length

$$\lambda_D = \sqrt{\frac{k_B T / 2}{e^2 \sum c_i Z_i^2 / \varepsilon\varepsilon_0}}$$

Thermal Energy

Electrostatic Energy density

- A rough measure of the characteristic length for potential decay

- Calculated with the ionic strength of the bulk fluid

E.G. 1M HCl @300K:

λ_D = 13.8 nm

1nM HCl@300K:

λ_D = 435 μm

Debye- Hückel Approximation

From:

$$(c_+ - c_-) = 2c_0 \sinh\left(\frac{zeU(x)}{k_B T}\right)$$

We define:

$$\tilde{U}(r) = -eZ_{ion}U(\vec{r})/k_B T$$

Substitution:

$$\nabla^2 U(\vec{r}) = \sum \frac{e}{\varepsilon} Z_{ion} c_{ion}(\vec{r})$$

We find:

$$\lambda^2 \nabla^2 \tilde{U}(\vec{r}) = \sinh^2(\tilde{U}(\vec{r}))$$

When: $\boxed{\tilde{U}(r) << 1}$

$$\lambda^2 \nabla^2 \tilde{U}(\vec{r}) \approx \tilde{U}^2(\vec{r})$$

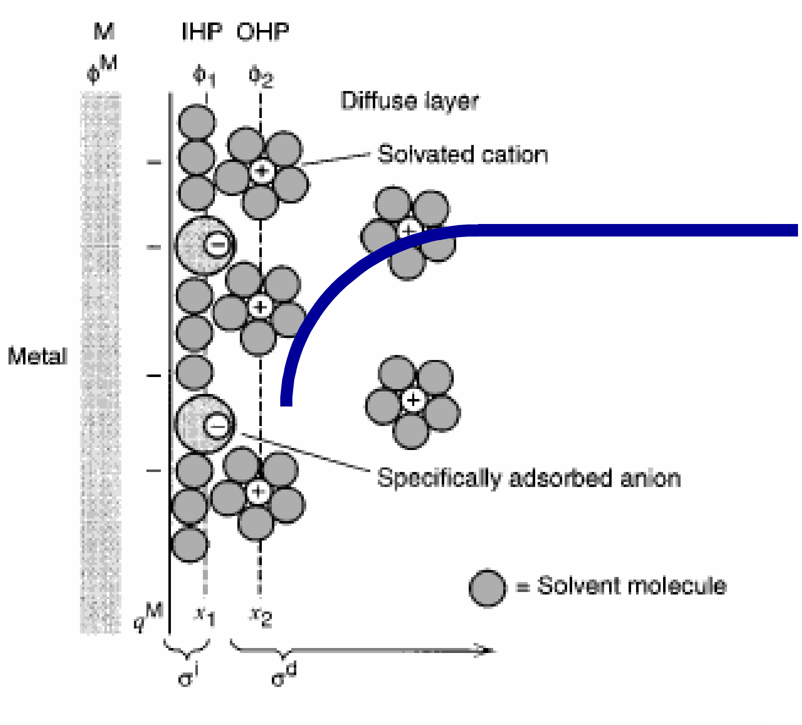
Approximated solution:

$$\tilde{U}(\vec{r}) \approx \tilde{U}_0 \exp(-\lambda x)$$

Electro-Osmotic Effect

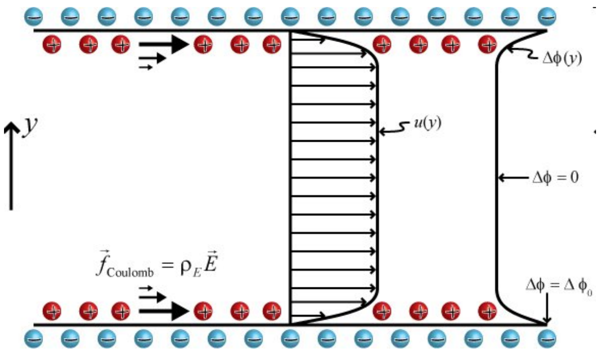
- In the diffuse layer, there is a net charge that moves according to external field

- Electric field induced ion flow also moves the fluid, following a flat velocity profile (plug flow)



$$v_{EOF} = \frac{zeE}{\eta}\lambda c_0$$

Electro-Osmotic Flow



www.kirbyresearch.com/.../etc/textbook/mae28.jpg

Plug-flow profile:

Very important for mixing and pumping in microdevices

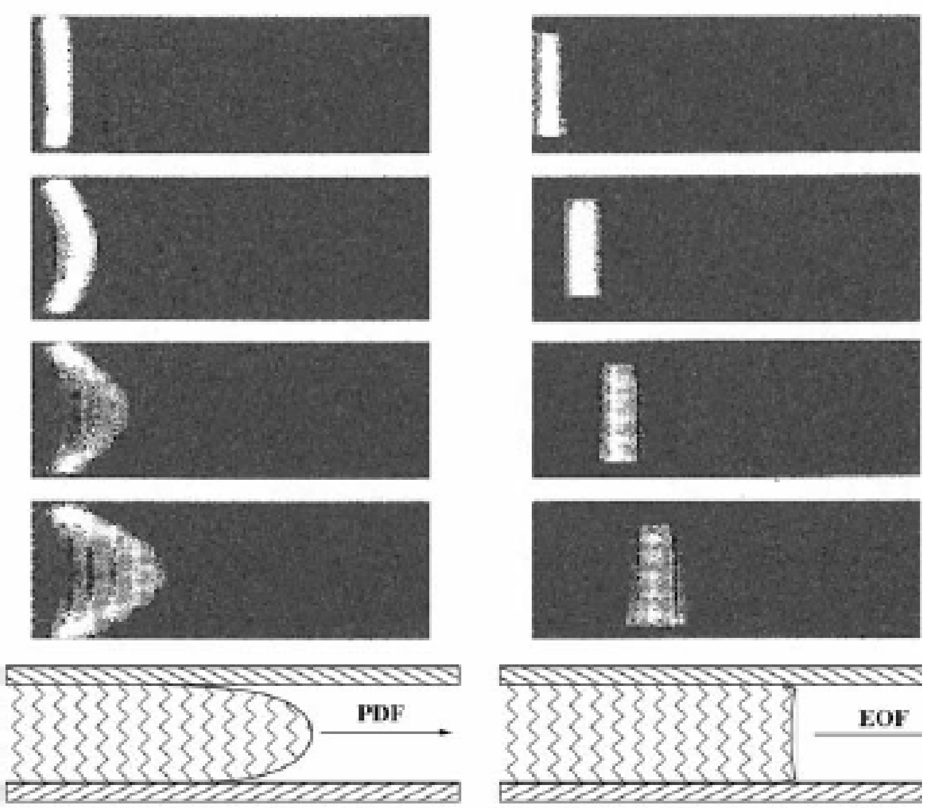


Fig. 3.42. Velocity profiles in pressure-driven and electroosmotic flow and expe mental observations recorded in 33-ms time frames

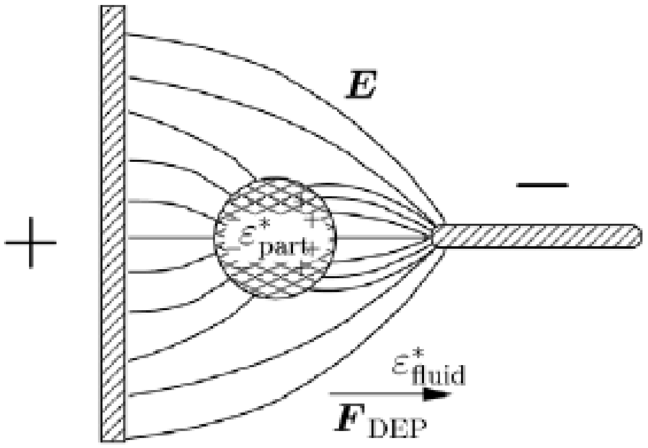
From: Jens Ducrée, •http://www.myfluidix.com/

Dielectrophoresis, etc

- Particles become polarized under electric field

- When E field is not uniform, there is a net force on particle

$$F \propto \underbrace{\alpha(\omega)}_{\text{Frequency dependent polarizability}}\underbrace{V}_{\text{Particle volume}}(\underbrace{\nabla E^2}_{\text{E field gradient}})$$



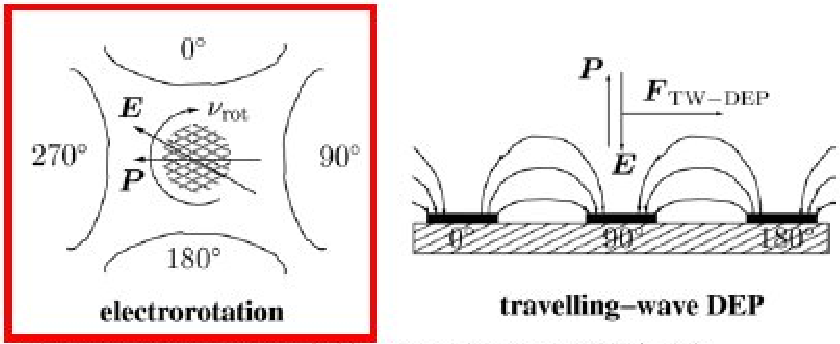


Fig. 3.47. Electrorotation (left) and travelling wave DEP (right)

From: Jens Ducrée, •http://www.myfluidix.com/

Additional Readings

- Jacob N. Israelachvili, ***Intermolecular and Surface Forces***, Chapt 12, Academic Press, 2nd Edition, 1992

- Jens Ducrée, online resources for micro- and nanofluidic technologies,Chap. 2.7 & 3.7 http://www.myfluidix.com/