# Hydrodynamic Interaction in Electrophoresis

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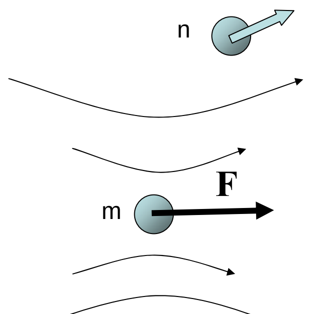
## Hydrodynamic Interaction



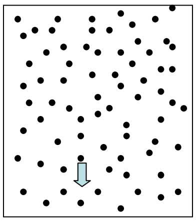

$$\mathbf{v}(\mathbf{r}) = \mathbf{H}(\mathbf{r}) \bullet \mathbf{F}$$

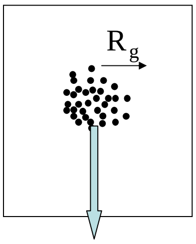
$$\mathbf{H}(\mathbf{r}) = \frac{\mathbf{I} + \hat{\mathbf{r}}\hat{\mathbf{r}}}{8\pi\eta r}$$

$$\mathbf{V}_{n} = \sum \mathbf{H}_{nm} \bullet \mathbf{F}_{m}$$

$$\mathbf{H}_{mn} = \mathbf{H}(\mathbf{r}_{mn})$$

# Hydrodynamic interaction is long ranged





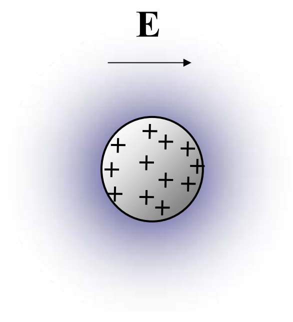

$$\mathbf{V}_n = \sum \mathbf{H}_{nm} \bullet \mathbf{F}_m$$

$$\mathbf{H}(\mathbf{r}) = \frac{\mathbf{I} + \hat{\mathbf{r}}\hat{\mathbf{r}}}{8\pi\eta r}$$

$$v_0 = \frac{mg}{6\pi\eta a}$$

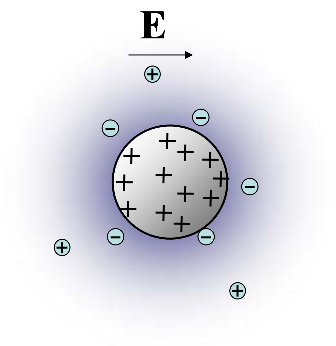
$$v = \frac{Nmg}{6\pi\eta R_g} = v_0\left(\frac{R_g}{a}\right)^{D-1}$$

# Electrophoresis




$$V = \mu E$$

# Naive theory for electrophoresis




Spherical particle of radius $a$

Total charge $Q$

Force $QE$

Velocity $V = \dfrac{QE}{6\pi\eta a}$

Surface potential $\zeta = \dfrac{Q}{4\pi\varepsilon a}$

$$V = \frac{2\varepsilon\zeta}{3\eta}E$$

The effect of charge screening and hydrodynamic interaction are totally ignored.

# "Standard theory" for the transport in ionic solution

Ionic solution=water+ion

water : dielectric liquid

ion : charged particle

$\mathbf{v}$ : water velocity

$\mathbf{v}_i$ : ion velocity

$c_i$ : number density

$\varphi$ : electric potential

Ion velocity

$$\xi_i(\mathbf{v}_i - \mathbf{v}) = -\nabla(k_B T \ln c_i + q_i\psi)$$

$$\frac{\partial c_i}{\partial t} = -\nabla \bullet (c_i \mathbf{v}_i)$$

Electric field

$$\varepsilon\nabla^2\psi = -\sum c_i q_i$$

Water velocity

$$\eta\nabla^2\mathbf{v} = \nabla p - \sum c_i \xi_i (\mathbf{v}_i - \mathbf{v})$$

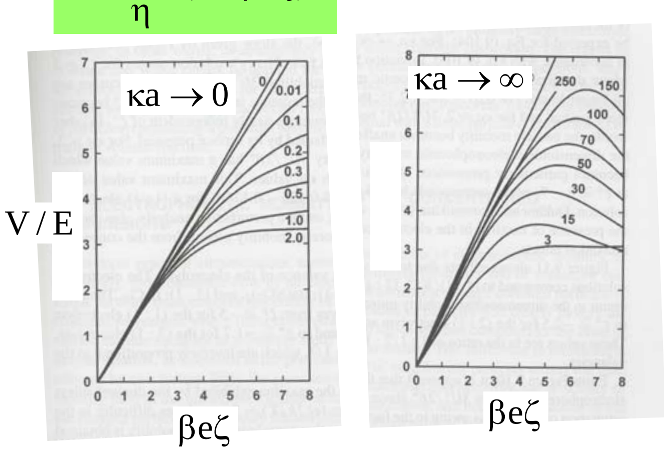
$$\nabla \bullet \mathbf{v} = 0$$

Smoluchowski equation

# Electrophoresis of Uniformly Charged Spherical Particle

$$V = \frac{\varepsilon\zeta}{\eta} f(\kappa a, \beta e\zeta) E$$

Obrien White 1978




$\kappa a \to 0$

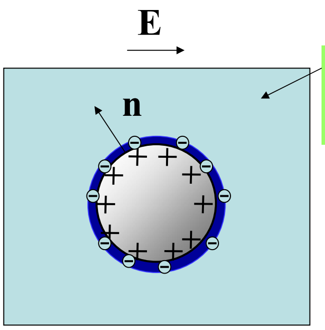
$$\frac{V}{E} = \frac{2\varepsilon\zeta}{3\eta}$$

$\kappa a \to \infty$

$$\frac{V}{E} = \frac{\varepsilon\zeta}{\eta}$$

# Important limit :thin double layer

$$\kappa a >> 1$$




Solution can be regarded as a conductive neutral fluid

Stokes equation $\eta \nabla^2 \mathbf{v} = -\nabla p$

$\nabla \bullet \mathbf{v} = 0$

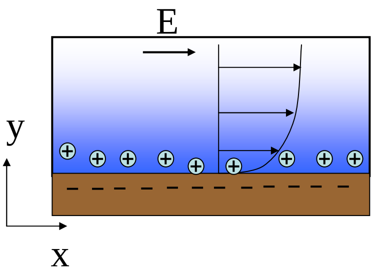
Electric field

$J = -\sigma_b \nabla \psi$ ⇨ $\nabla^2 \psi = 0$

$\nabla \bullet J = 0$

At the outer boundary of the sphere $\mathbf{n} \bullet \nabla \psi = 0$

# Smoluchowsii's slip velocity




$$v_x(y) \rightarrow U_s$$

$$U_s = -\frac{\varepsilon\zeta}{\eta}E$$

Slip velocity

Smoluchowskii ~1910

$$\eta\frac{d^2 v_x}{dy^2} = -\sum c_i q_i E$$

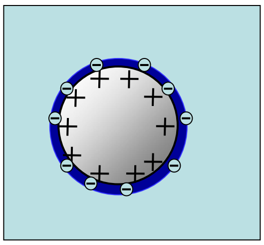
$$\sum c_i q_i = -\varepsilon\frac{d^2\psi}{dy^2}$$

$$\eta\frac{d^2 v_x}{dy^2} = \varepsilon\frac{d^2\psi}{dy^2}E$$

⇩

$$\eta(v_x(y) - v_x(0)) = \varepsilon(\psi(y) - \psi(0))E$$

# Conventional equations for thin double layer limit



Bulk equaion

$$\nabla^2\varphi = 0$$

$$\eta\nabla^2\mathbf{v} = -\nabla p$$

$$\nabla\bullet\mathbf{v} = 0$$

Boundary condition

$$\mathbf{n}\bullet\nabla\varphi = 0$$

$$\mathbf{v} = \mathbf{V} + \frac{\varepsilon\zeta}{\eta}\nabla_t\varphi$$

$$\mathbf{V} = \frac{\varepsilon\zeta}{\eta}\mathbf{E}$$

$$\mathbf{E}(\mathbf{r}) = \left[1 - \frac{1}{2}\left(\frac{a}{r}\right)^3\left(3\frac{\mathbf{rr}}{r^2} - \mathbf{I}\right)\right]\bullet\mathbf{E}^\infty$$

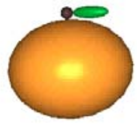
$$\mathbf{v} = \frac{1}{2}\left(\frac{a}{r}\right)^3\left(3\frac{\mathbf{rr}}{r^2} - \mathbf{I}\right)\bullet\mathbf{V}$$

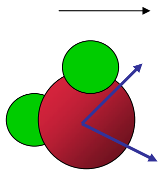
# Particle Simulator MIKAN
## -Microhydrodynamic Kinetic Analyzer-

Masato Makino

- Boundary element method
- Rigig particles
- Arbitrary shape and charge distribution

$\mathbf{E}^{\infty}$ :Electric field





$\mathbf{F}$ :External force

$\mathbf{T}$ :Torque

$k_B T$ :Brownian motion

Velocity $$\mathbf{V} = \mathbf{a} \bullet \mathbf{F} + \mathbf{b} \bullet \mathbf{T} + \mathbf{p} \bullet \mathbf{E}^{\infty} + \Delta \mathbf{V}$$

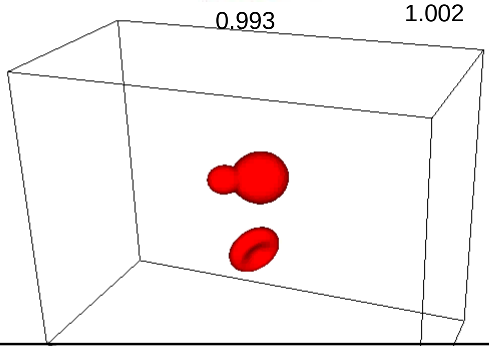
Angular velocity $$\mathbf{\Omega} = \mathbf{b} \bullet \mathbf{F} + \mathbf{c} \bullet \mathbf{T} + \mathbf{q} \bullet \mathbf{E}^{\infty} + \Delta \mathbf{\Omega}$$

# Simple result for uniformly charged particle

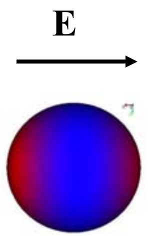
Morrison's theorem Morrison 1970

Uniformly charged particle translates uniformly

$$\mathbf{V} = \frac{\varepsilon\zeta}{\eta}\mathbf{E}$$

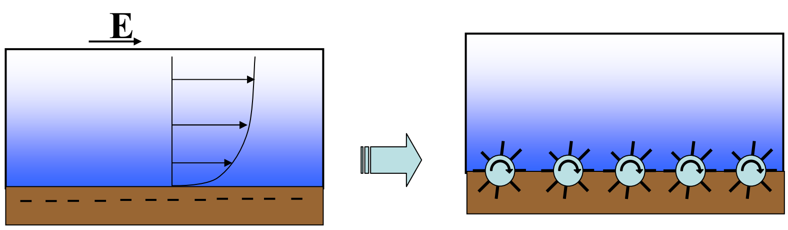
## Complex Result for Non-uniformly Charged Particle




$$\zeta(\theta) = \zeta_0 (3\cos^2\theta - 1)$$

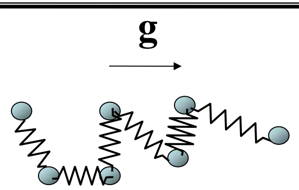
Place particle at orgin in random

## Surface Slippage Determines the Electrophoresis




$$\mathbf{v} - \mathbf{V} = -\frac{\varepsilon\zeta}{\eta}\mathbf{E}$$

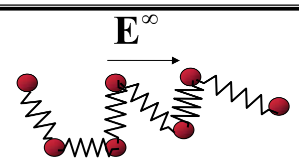
# Hydrodynamic interaction in charged polymers




Hydrodynamic interaction for neutral polymers

$$\mathbf{V}_i = \sum_j \mathbf{H}_{ij} \bullet (\mathbf{F}_j + m\mathbf{g})$$

$$V \approx \frac{Nmg}{6\pi\eta R_h} \propto \sqrt{N}$$




Electrophoresis of charged polymers

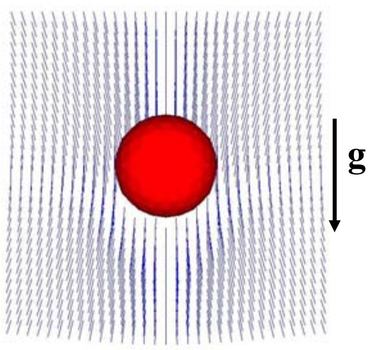
$$\mathbf{V}_i = \sum_i \mathbf{H}_{ij} \bullet (\mathbf{F}_j + q_j \mathbf{E}^{\infty})$$

$$V \approx \frac{NqE}{6\pi\eta R_h} \propto \sqrt{N}$$

Correct answer is

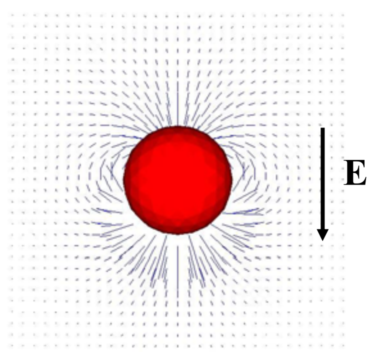
$$\mathbf{V} = \frac{\varepsilon\zeta}{\eta} \mathbf{E}^{\infty} \propto \text{ independent of N}$$

# Velocity field in sedimentation and electrophoresis




Sedimentation

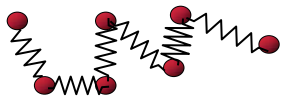
$$v(r) \propto \frac{1}{r}$$

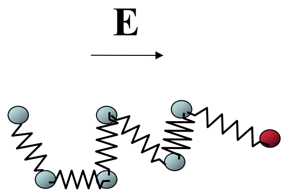



Electrophoresis

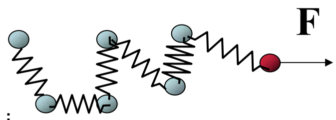
$$v(r) \propto \frac{1}{r^3}$$

# Rouse Zimm model for charged polymer






$$\mathbf{V}_i = \sum_j \mathbf{H}_{ij} \bullet \mathbf{F}_j + \mu_i \mathbf{E}$$

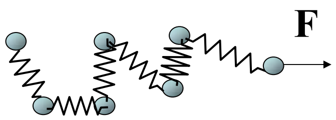



$\mathbf{F}_i$ : force

$\mu_i = \dfrac{\varepsilon \zeta_i}{\eta}$ : surface potential of bead i

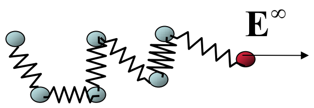
# Approximate theory

$$\mathbf{V}_i = \sum_j \mathbf{H}_{ij} \bullet \mathbf{F}_j + \mu_i \mathbf{E}^{\infty}$$




$$V = \frac{1}{\eta a} \sum_{j=0}^{N} \frac{1}{|i-j|^{1/2}} f_j \qquad i = 0,1,\ldots N$$

$$\sum_{j=0}^{N} f_j = F \qquad V \approx \frac{F}{\eta a \sqrt{N}}$$

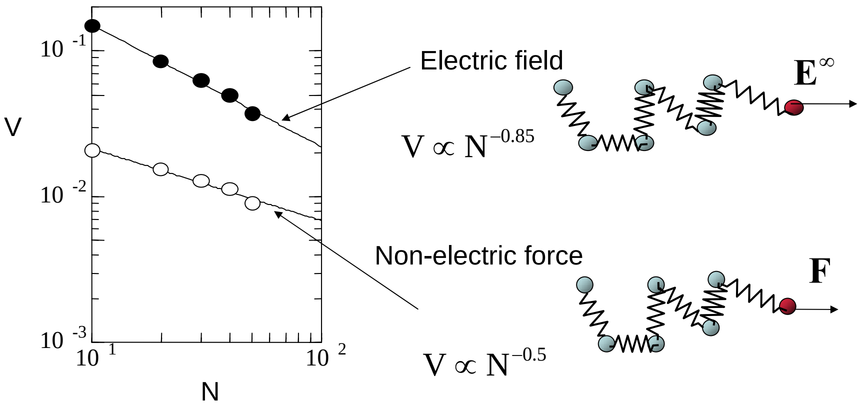



$$V = \frac{1}{\eta a} \sum_{j=0}^{N} \frac{1}{|i-j|^{1/2}} f_j + \delta_{i0} \mu E$$

$$\sum_{j=0}^{N} f_j = 0$$

## Result of simulation

$$\mathbf{V}_i = \sum_j \mathbf{H}_{ij} \bullet \mathbf{F}_j + \mu_i \mathbf{E}^\infty$$



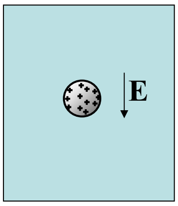

## Reciprocal relations

## Reciprocal relation

The conventional equation fails to explain the sedimentation potential

Electrophoresis

$\mathbf{E} \Rightarrow \mathbf{V}$

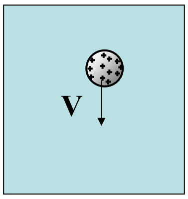



$V = \mu E$

Sedimentation potential

$\mathbf{V} \Rightarrow \mathbf{E}$

$\mathbf{F} \Rightarrow \mathbf{J}$




$J = \mu F$

## Electro-hydrodynamic interaction

$$\mathbf{V}_i = \sum_j \mathbf{H}_{ij} \bullet \mathbf{F}_j + \mu_i \mathbf{E}$$

$$\mathbf{J} = \sigma \mathbf{E} + \sum_i \mu_i \mathbf{F}_i$$