Dynamics of charged-particles dispersions:

From large colloids to nano-sized bioparticles and electrolyte ions

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Books and Lecture Notes

1. W.B. Russel, D.A. Saville, and W.R. Schowalter, ***Colloidal Dispersions***, Cambridge University Press (1989)
2. E. Guazelli and J.F. Morris, ***A Physical Introduction to Suspension Dynamics***, Cambridge University Press (2012)
3. G. Nägele, ***Colloidal Hydrodynamics***, in Proceedings of the International School of Physics, "Enrico Fermi", Course 184 "Physics of Complex Colloids", ed. by C. Bechinger, F. Sciortino and P. Ziherl, (IOS, Amsterdam; SIF, Bologna) pp. 507 – 601 (2013)
4. J.-L. Barrat and J.-P. Hansen, ***Basic Concepts for Simple and Complex Fluids***, Cambridge University Press (2003)
5. J.H. Masliyah and S. Bharracharjee, ***Electrokinetic and Colloid Transport Phenomena***, Wiley - Interscience (2006)
6. H. Ohshima, ***Theory of Colloid and Interfacial Electric Phenomena***, Interface Science and Technology - Volume 12, Elsevier (2006)
7. R.J. Hunter, ***Foundations of Colloid Science***, Oxford University Press (1989)
8. R.J. Hunter, ***Zeta Potential in Colloid Science***, Academic Press (1988)
9. J.K.G. Dhont, ***An Introduction to Dynamics of Colloids*****,** Elsevier, Amsterdam (1996)
10. G. Nägele, ***The Physics of Colloid Soft Matter:*** *Lecture Notes 14*, Polish Academy of Sciences Publishing, Warsaw (2004)
11. G. Nägele, ***On The Dynamics and Structure of Charge - Stabilized Colloidal Suspensions****,* Physics Reports 272, pp. 215-372 (1996)

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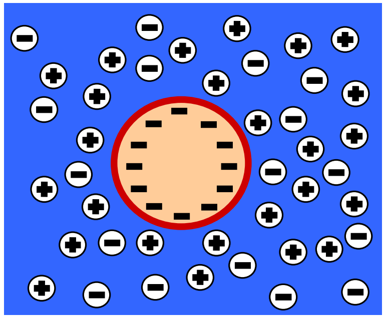
1. Introduction & Motivation

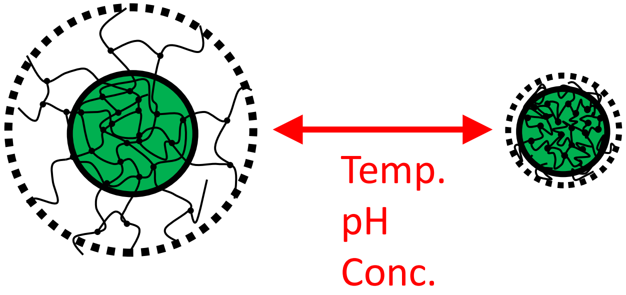
- Examples of dispersions
- Direct particle interactions
- Brownian forces
- Inertia - free dynamics
- Hydrodynamic effects: examples

1.1 Examples of dispersions

- Micron – sized charge-stabilized colloidal particles: 40 nm < ∅ < 5 μm

$|Q_{bare}| \approx 10 - 20\,000$ e





- silica
- goldsol
- PMMA

...

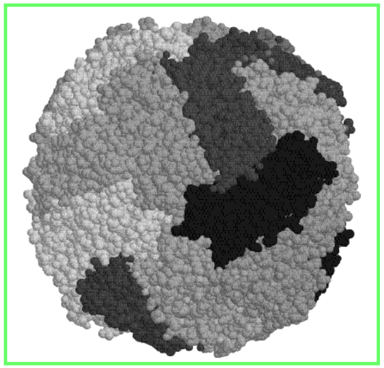
- Ionic microgel particles

(solvent: water, polar fluid)

Products / Applications: dispersion paints, pharmaceuticals, food stuff, cosmetics, waste water, drug delivery (microgels), …

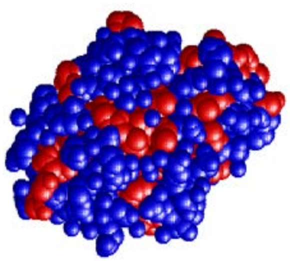
- Nanometer - sized globular proteins in (salty) water ($|Q_{bare}| \approx 8 - 30$ e)

Apoferritin

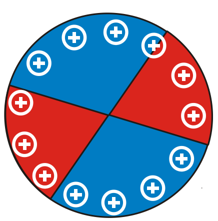


← 13 nm →

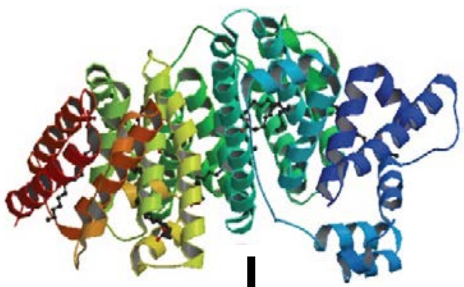
Hen-egg lyzozyme

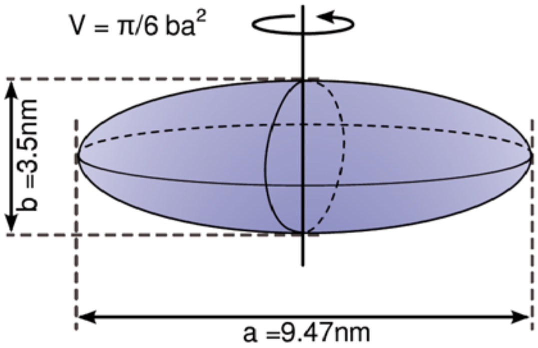


← 6 nm →

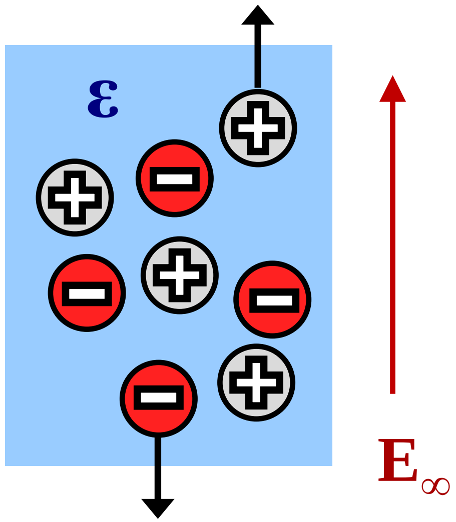


Bovine serum albumin (BSA)





- Strong electrolyte solution (e.g., NaCl in water)



 $\varnothing(Cl^-)$ = 0.36 nm

 $\varnothing(Na^+)$ = 0.55 nm

$$u_{\alpha\beta}(r) = u^S_{\alpha\beta}(r) + u^C_{\alpha\beta}(r)$$

$$\frac{u^C_{\alpha\beta}(r)}{k_B T} = L_B \frac{z_\alpha z_\beta}{r}, \quad r > \left(a_\alpha + a_\beta\right)$$

$$L_B = e^2/(\varepsilon k_B T) \approx 0.7\text{nm}$$

(Bjerrum length)

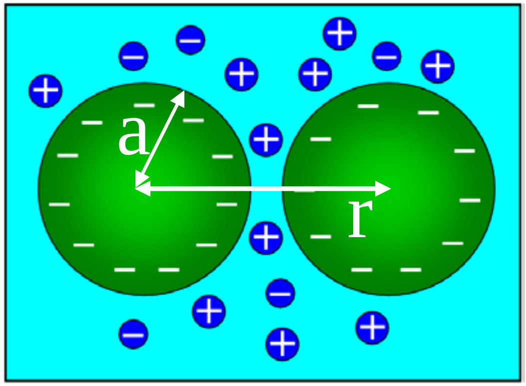
$$\Lambda \approx \Lambda_0 - \text{const} \times \sqrt{n_T}$$

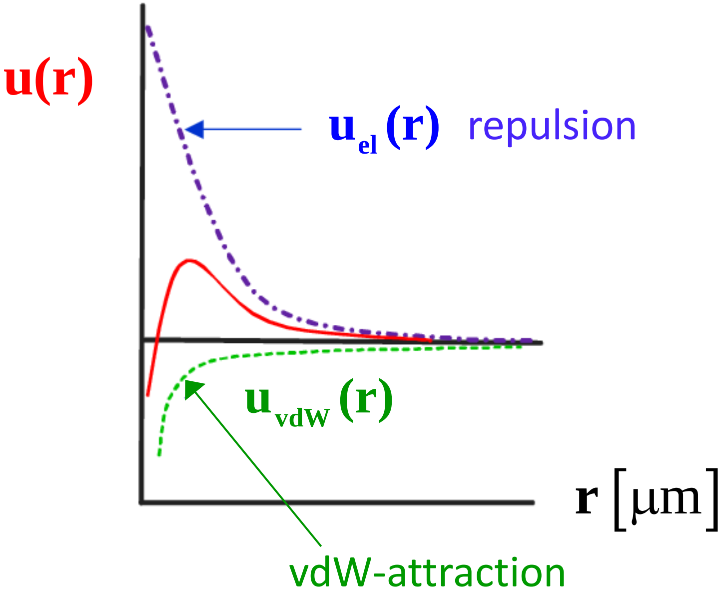
Falkenhagen - Onsager limiting law for conductivity

valid only for $n_T = n_+ + n_- < 0.01$ mol /litre

1.2 Direct particles interactions

- Dressed macroion model and DLVO theory





$$\beta u(r) = L_B Z^2 \left(\frac{\exp[\kappa a]}{1+\kappa a} \right)^2 \frac{\exp[-\kappa r]}{r}$$

effective charge number $Z < |Q_{bare}| / e$

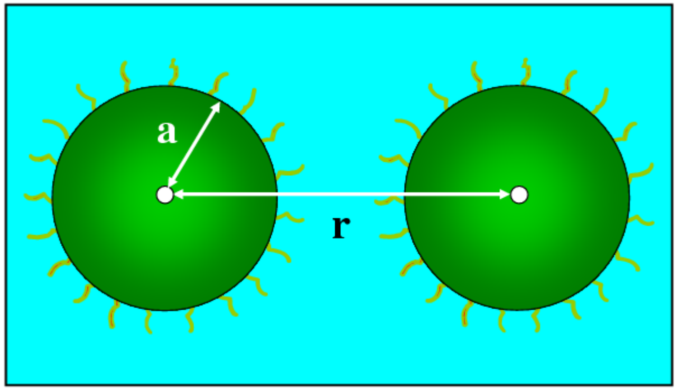
$u(r) \approx u_{el}(r)$ for $|Z| >> 1$

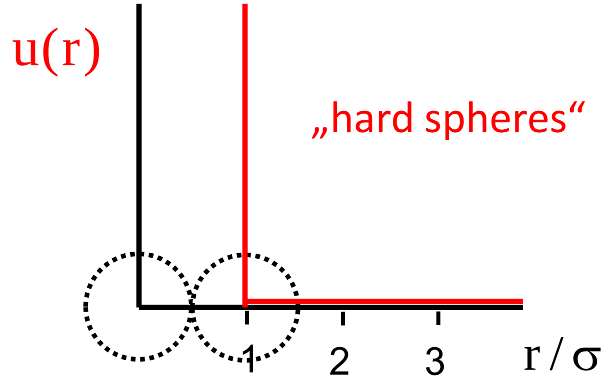
$$\kappa^2 = 4\pi L_B \left(n|Z| + 2n_s\right) / (1-\phi)$$

- Tuning of range and strength of effective pair potential by changing salt content & solvent
- Microion electrokinetic effects disregarded in this model !

- For comparison: neutral colloidal hard spheres

Sterically stabilized particles:





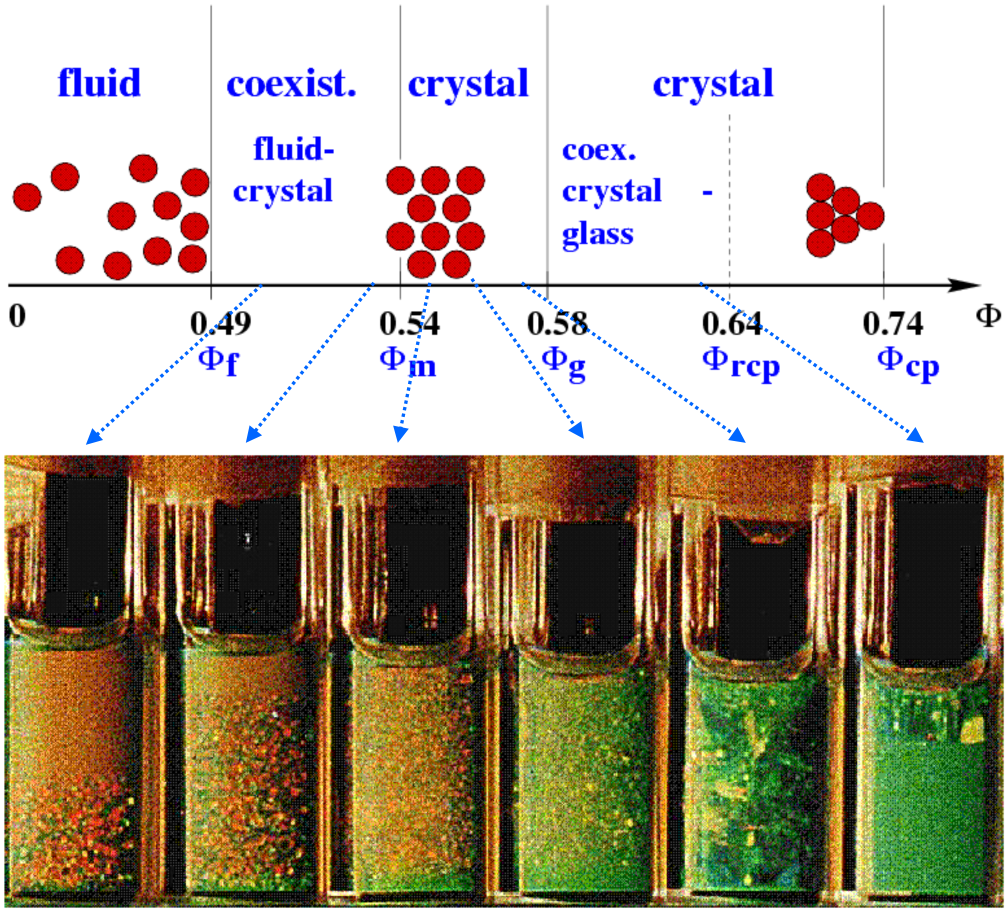
$$u(r) = \begin{cases} \infty\,, & r < \sigma = 2a \\ 0\,, & r > \sigma \end{cases}$$

- Pairwise additive N-particle eff. potential energy (**approximation** for CS, not for HS)

$$V_N\left(\mathbf{R}^N\right) = \sum_{i<j}^{N} u\left(\left|\mathbf{R}_i - \mathbf{R}_j\right|\right) = \sum_{i<j}^{N} u\left(R_{ij}\right)$$

$$\mathbf{R}^N = X = \{\mathbf{R}_1, \dots, \mathbf{R}_N\}$$

Phase behavior of colloidal hard - sphere dispersion



$$\phi = \frac{N v_{sphere}}{V_{system}} = \frac{4\pi}{3} n a^3$$

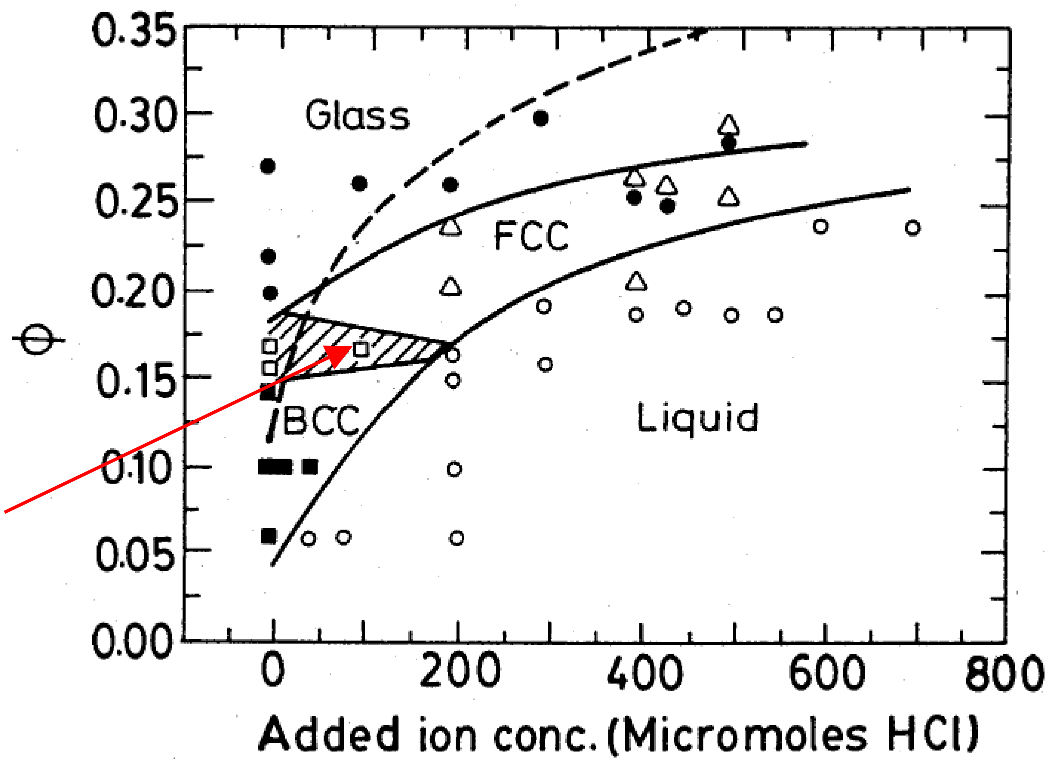
$$\phi_{cp}^{fcc} = \pi / \sqrt{18}$$

Kepler: 1611

Hales: 1998

Pusey & van Megen, Nature 320, 1986

Phase behaviour of a charged - spheres system (silica spheres)

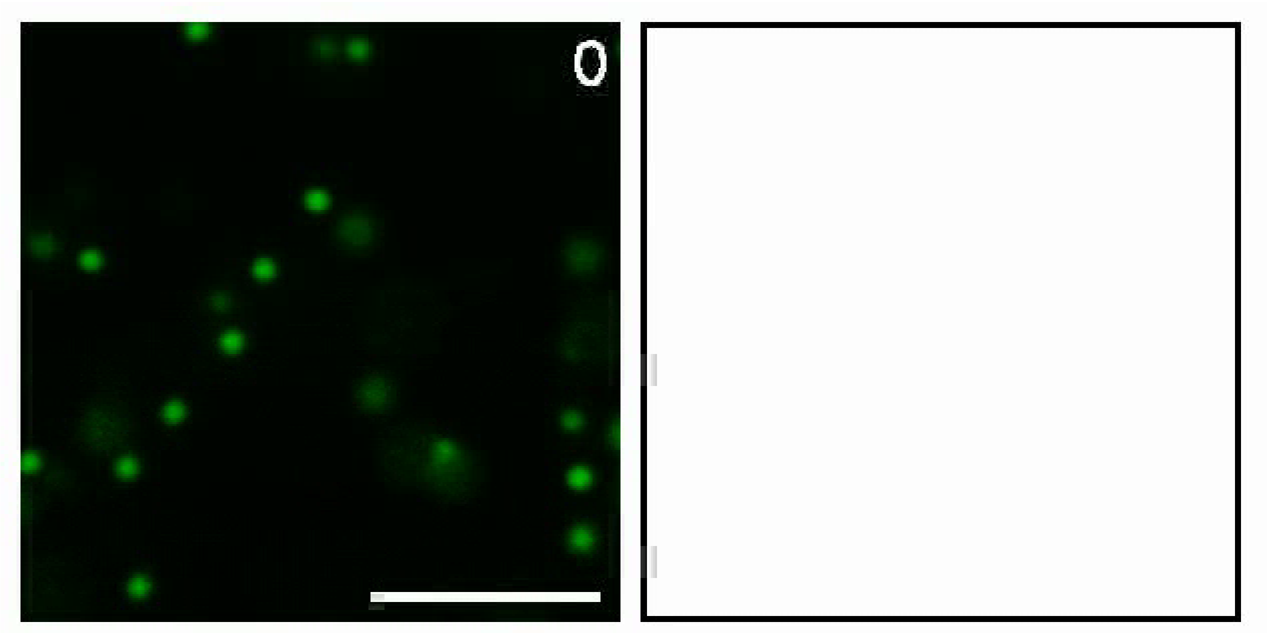


fcc – bcc coexistence

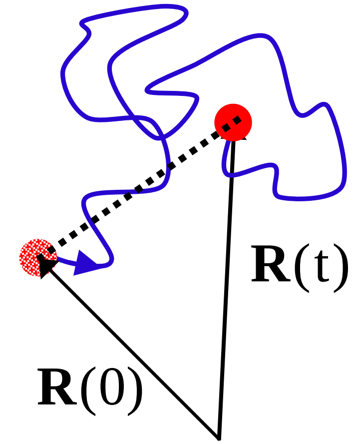
Sirota et al.
PRL 62, 1989

- BCC phase at low salinity (8 next neigbours), FCC phase at higher salinity (12 n.n.)
- Metastable glass - like phase at higher volume fractions (polydispersity)

1.3 Brownian forces



← 10μm →



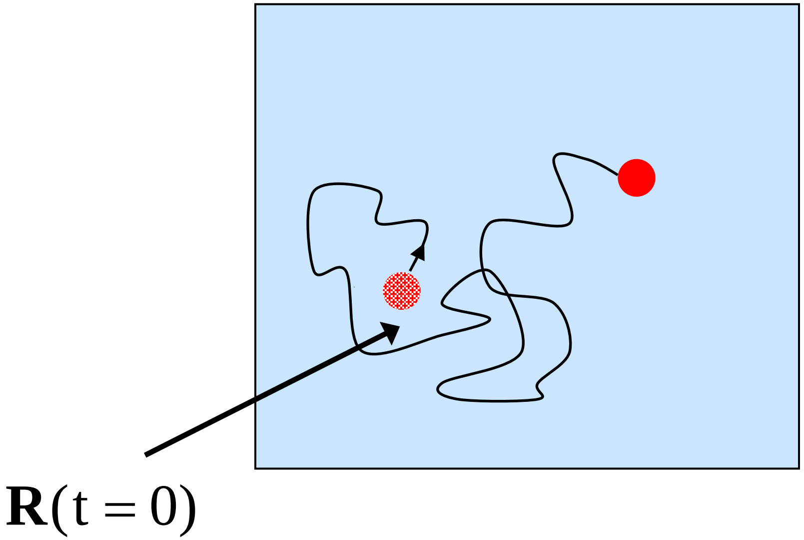
$$\langle \mathbf{R}(t) - \mathbf{R}(0) \rangle = 0$$

$$W(t) = \frac{1}{6}\left\langle [\mathbf{R}(t) - \mathbf{R}(0)]^2 \right\rangle$$

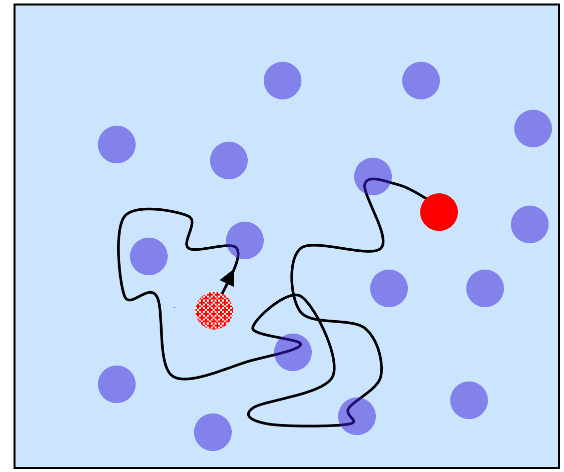
Mean-squared displacement

Movie: E.R. Weeks, Austin

Self - diffusion of colloids (Brownian particles)



Single - sphere diffusion

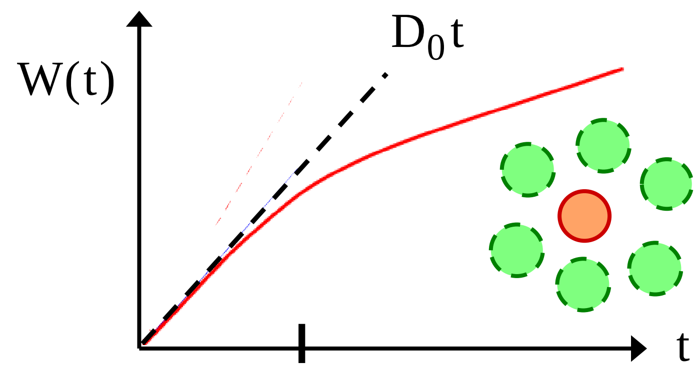


direct interactions only

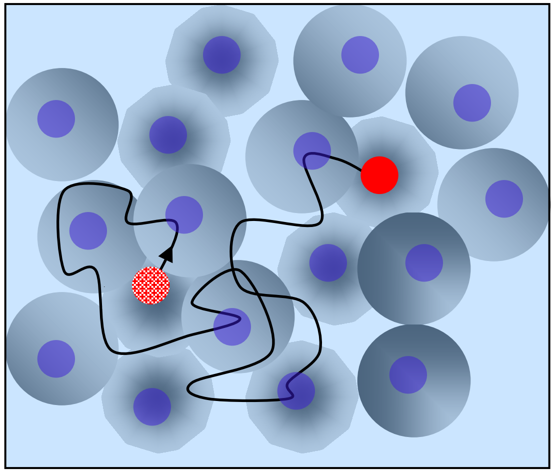
$$W(t) = \left\langle \left[\mathbf{R}(t) - \mathbf{R}(0)\right]^2 \right\rangle / 6 = D_0 t$$

$$D_0 = \frac{k_B T}{6\pi\eta_0 a} = \frac{k_B T}{\zeta_0}$$

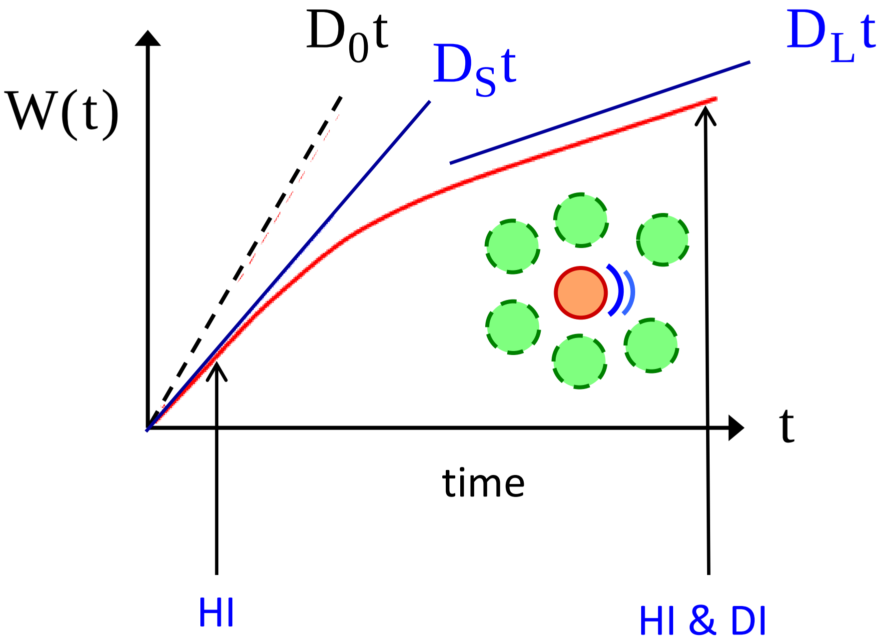
Stokes
Einstein
Sutherland



diffusion relaxation time → $\tau_D = a^2 / D_0$

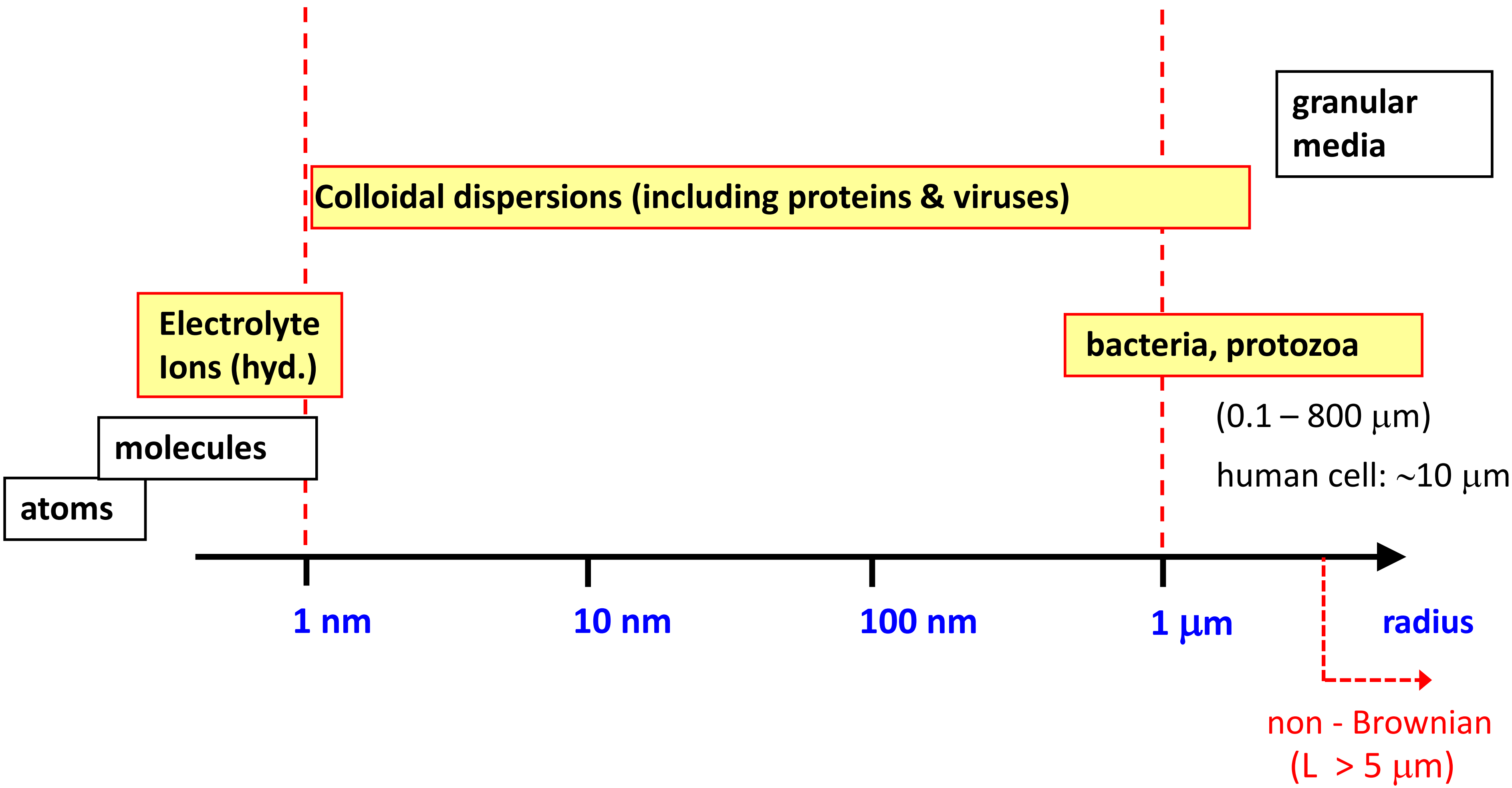


$$D_L < D_S < D_0$$



➢ Self – diffusion in general slowed down by hydrodynamic interaction (HIs)

1.4 Inertia - free dynamics



- Colloids, proteins and most bacteria share common **inertia - free** hydro-dynamics

Inertia – free particle dynamics

- quasi - inertia free motion on coarse-grained colloidal time- and length scales

$$M\frac{d\langle V\rangle(t)}{dt} \approx -\zeta_0 \langle V\rangle(t)$$

- momentium relaxation time

$$\Delta t >> \tau_B = \frac{M}{\zeta_0} \approx 10^{-8} \text{ sec}$$

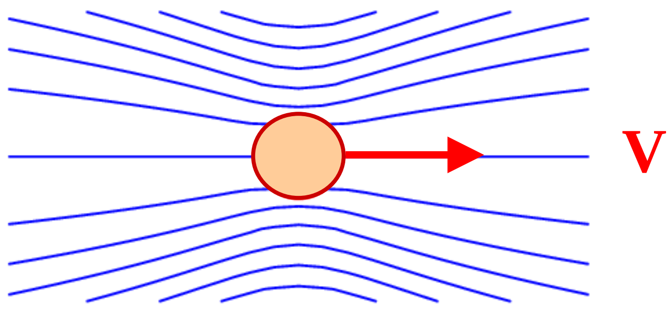
$$\Delta x >> l_B = \sqrt{D_0 \tau_B} \approx 10^{-4} \sigma$$

"stopping distance"

Rhodospirillum bacteria (length $\sigma \approx 5$ μm)

Low-Reynolds number solvent flow

- Inertial forces tiny as compared to friction forces: **Reynolds - # << 1**
- Instantaneous flow profile restructuring around moving particle



$$\mathrm{Re} = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{\rho_f \, aV}{\eta_0}$$

in water:

wale:	10^8
human swimmer:	10000
colloid particle:	0.0001
bacteria /cells:	0.00001

$$\nabla \cdot \mathbf{u}(\mathbf{r}) = 0$$

incompressibility

$$-\nabla p(\mathbf{r}) + \eta_0 \Delta \mathbf{u}(\mathbf{r}) + \mathbf{f}^e(\mathbf{r}) = \mathbf{0}$$

linear quasi-staticStokes equation

Inertia-free force balance

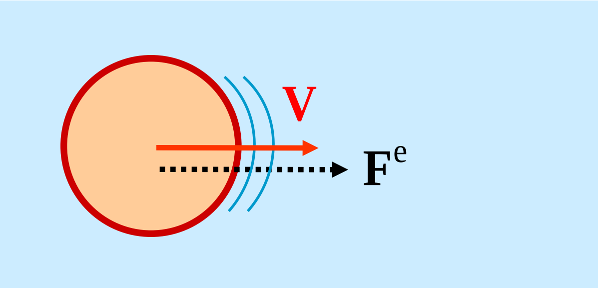
Implication: linear particle hyd. force – velocity relations

- Sphere with stick (no-slip) BC translating ín quiescent infinite fluid

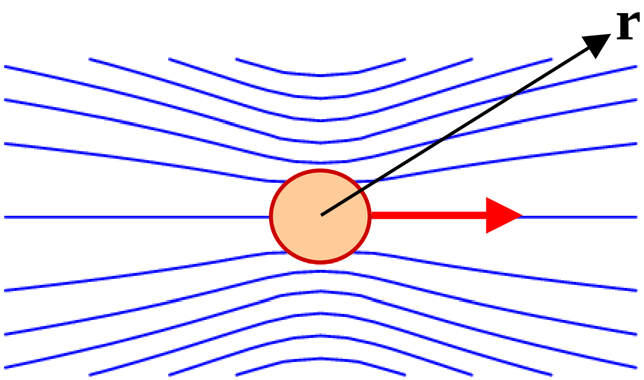
$$\boxed{\mathbf{V} = \mu_0^t \, \mathbf{F}^e} \qquad \mu_0^t = \frac{1}{6\pi\eta_0 a}$$

translational mobility

(6π → 4π : perfect slip)



$$\boxed{D_0 = k_B T \mu_0^t}$$



$$\mathbf{u}(\mathbf{r}) \sim 1/r$$

$$p(\mathbf{r}) \sim 1/r^2$$

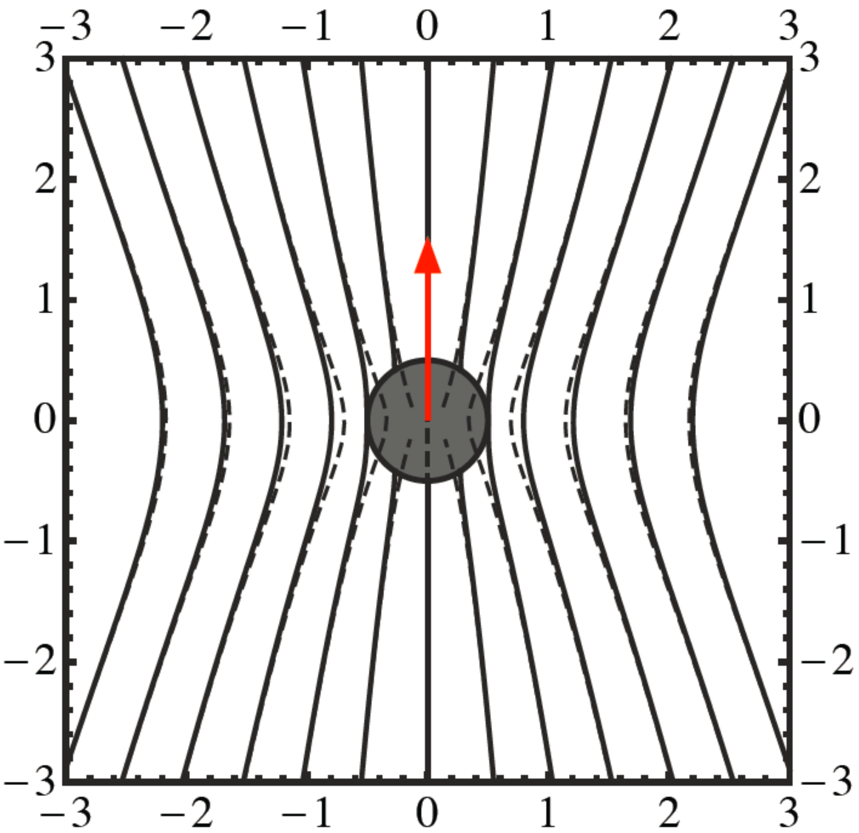
long-range decay

$$\mathbf{u} \times d\mathbf{r} = \mathbf{0} \quad \Rightarrow \quad \frac{dx}{u_x} = \frac{dy}{u_y} = \frac{dz}{u_z}$$

stream lines = path lines when stationary flow

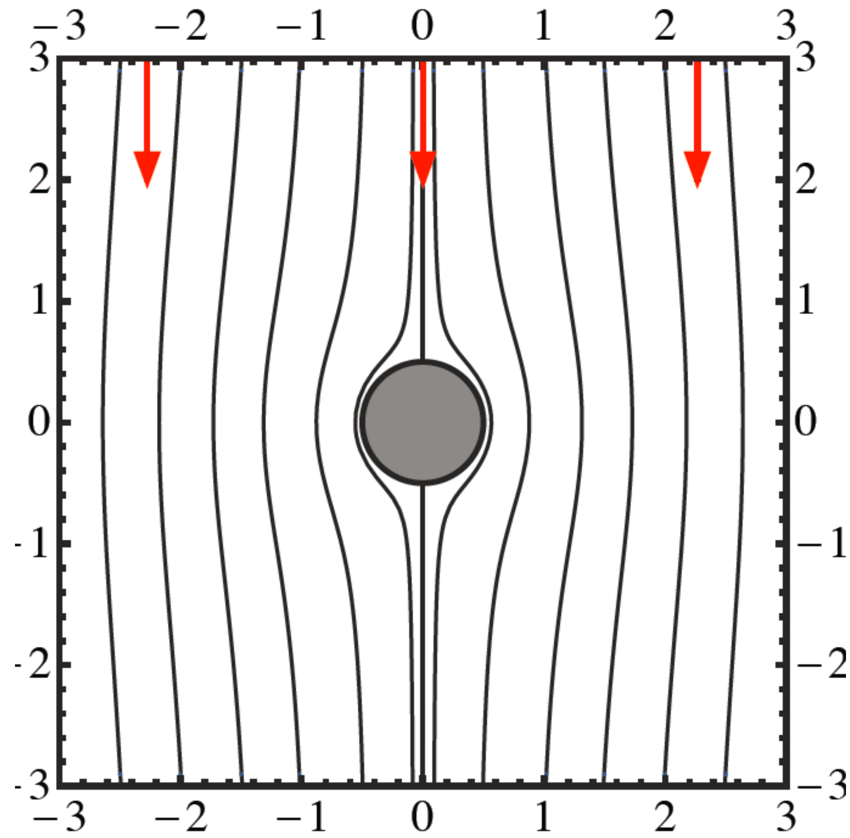
- Sphere in quiescent, infinite fluid, stick BC

$$\mathbf{u}_\infty = \mathbf{0}$$



- Sphere stationary (rest frame)

$$\mathbf{u}_\infty = -\mathbf{V}$$

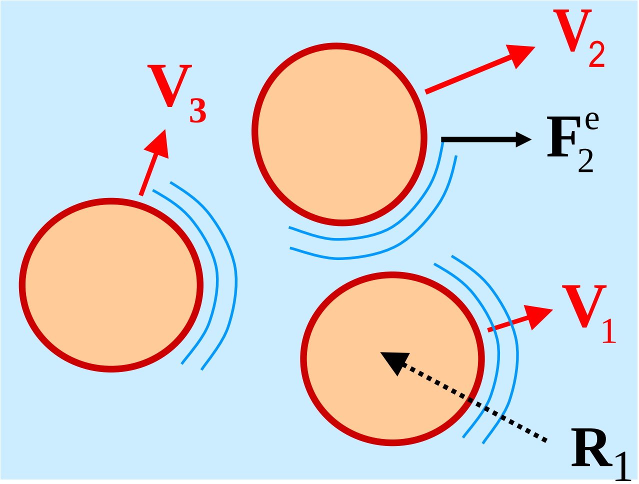


$$\mathbf{u}(a\hat{\mathbf{r}}) \cdot \hat{\mathbf{n}} = 0 \qquad \mathbf{u}(a\hat{\mathbf{r}}) \cdot \hat{\mathbf{t}} = 0$$

N freely rotating spheres: hydrodynamic interactions (HIs)

$$\mathbf{V}_i = \sum_{j=1}^{N} \boldsymbol{\mu}_{ij}^{tt}(X) \cdot \mathbf{F}_j^e$$

translational
3×3 mobility tensors



$$V = \mu^{tt}(X) \cdot F^e$$

mobility problem

$$\mathbf{D}_{ij}^{tt} = k_B T \boldsymbol{\mu}_{ij}^{tt}$$

diffusivity matrix

$$X = \{\mathbf{R}_1, \ldots, \mathbf{R}_N\}$$

$$\mathbf{V} = (\mathbf{V}_1, \ldots, \mathbf{V}_N)^T$$

$$\mu^{tt} = \begin{pmatrix} \boldsymbol{\mu}_{11}^{tt} & \cdots & \boldsymbol{\mu}_{1N}^{tt} \\ \vdots & & \vdots \\ \boldsymbol{\mu}_{N1}^{tt} & \cdots & \boldsymbol{\mu}_{NN}^{tt} \end{pmatrix}$$

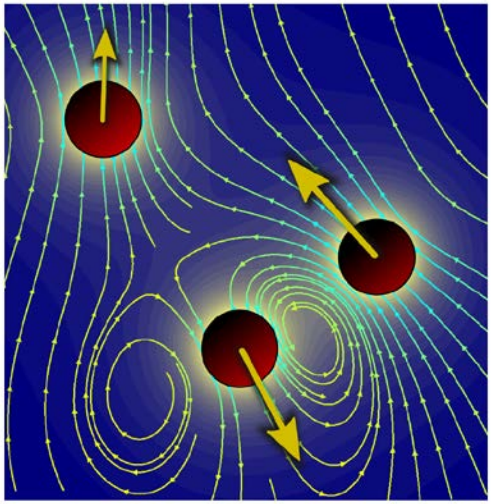
3N x 3N matrix
symmetric & pos. definite

$$\boldsymbol{\mu}_{ij}^{tt}(\mathbf{X}) = \boldsymbol{\mu}_{ij}^{RP}(\mathbf{R}_i - \mathbf{R}_j) + \Delta\boldsymbol{\mu}_{ij}(X)$$

far-field HI: $\sim O(r^{-1})$

near-field HI: $\sim O(r^{-4})$

- HI acts quasi – instantaneously on colloidal time scales
- near - field part **non pairwise additive**



- Moblity tensors required as input in calculations of colloidal, protein, and electrolyte transport properties
- Flow pattern of **u**(r), p(r) itself not needed

$$D_S = \frac{k_B T}{3} \mathrm{Tr} \left\langle \boldsymbol{\mu}_{11}^{tt} \right\rangle_{eq}$$ - self-diffusion coefficient $\boldsymbol{\mu}_{11}^{tt} \sim O(r^{-4})$

$$\mathbf{V}_{sed} = \left\langle \sum_{p=1}^{N} \boldsymbol{\mu}_{1p}^{tt}(X) \right\rangle_{eq,ren} \cdot \mathbf{F}^e$$ - mean sedimentation velocity $\boldsymbol{\mu}_{12}^{tt} \sim O(r^{-1})$ (**renormalization** required)

- ⟨…⟩ average over homogeneous and isotropic particle ensemble

Pure configuration - space decription for t $\gg \tau_B$

Overdamped Langevin-Eq.

$$M\dot{\mathbf{V}}_i(t) = 0 = \mathbf{F}_i^I + \mathbf{F}_i^h + \mathbf{K}_i^R$$

For Brownian particles:
Random force

Dynamic simulations

Generalized Smoluchowski Eq.

$$\frac{\partial}{\partial t}P(X,t) + \sum_{i=1}^{N} \nabla_i \cdot \left[\mathbf{v}_i(X,t)\,P(X,t)\right] = 0$$

PDF

coarse-grained velocity from
force balance

Theoretical calculations

- Moblity tensors are input in N – particle diffusion equation (Smoluchowski)

$$\frac{\partial}{\partial t} P(X,t) = k_B T \sum_{i,j=1}^{N} \nabla_i \cdot \boldsymbol{\mu}_{ij}^{tt}(X) \cdot \left[\nabla_j - \beta \mathbf{F}_j^I - \beta \mathbf{F}_j^e \right] P(X,t)$$

Irreversibility (Brownian motion ∝ T)

pdf

- Positive definiteness of mobility matrix implies for zero external forces & flow

$$P(X, t \to \infty) \to P_{eq}(X) \propto \exp\left[-\beta V_N(X)\right] \qquad \mathbf{F}_j^I = -\nabla_j V_N(X)$$

G. Nägele, Phys. Rep. **272** (1996) and J. Dhont, *An Introduction to Dynamics of Colloids*, Elsevier (1996)

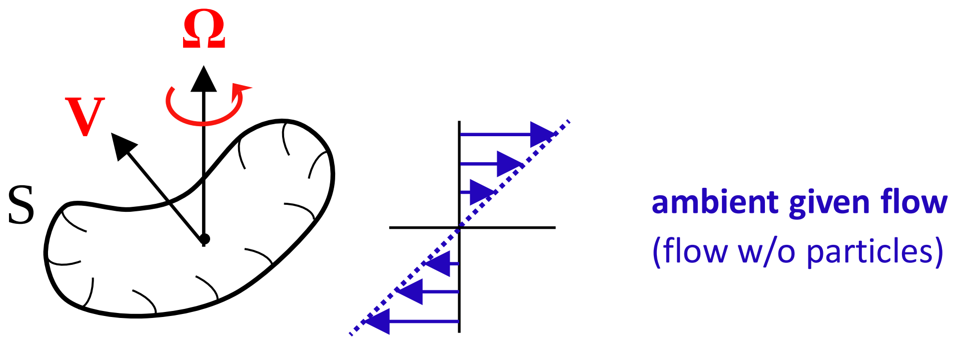
1.5 Low – Reynolds - number flow examples

- Kinemaric reversibility (ignore Brownian motion for time being)

$$-\nabla p(\mathbf{r}) + \eta_0 \nabla^2 \mathbf{u}(\mathbf{r}) + \mathbf{f}^e(\mathbf{r}) = 0 \qquad \nabla \cdot \mathbf{u}(\mathbf{r}) = 0 \qquad \mathbf{r} \in V_{fl}$$

$$\mathbf{u}(\mathbf{r})\big|_S = \mathbf{V} + \mathbf{\Omega} \times \left(\mathbf{r} - \mathbf{R}_p\right)\big|_S$$

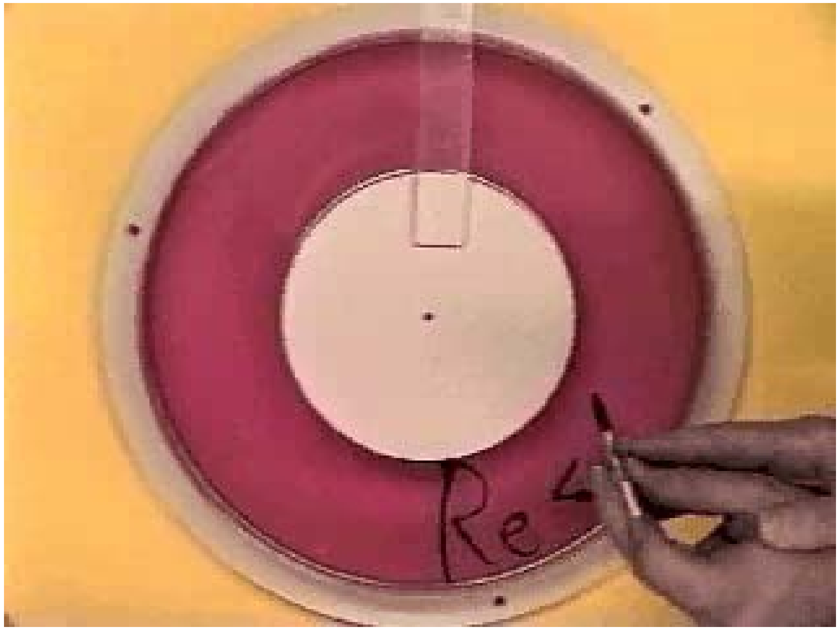
$$\mathbf{u}(\mathbf{r} \to \infty) = \mathbf{u}_\infty(\mathbf{r})$$



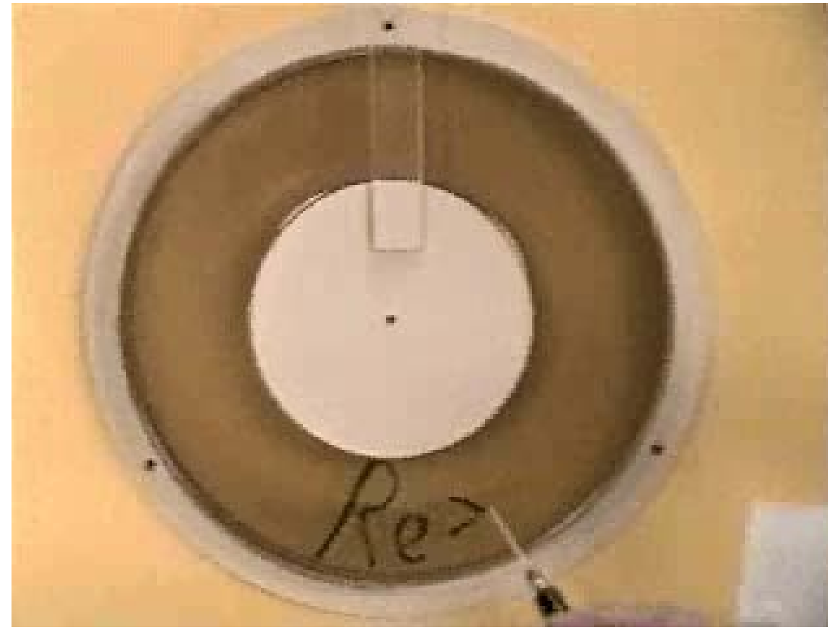
Since linear boundary value problem (BVP):

$$\left\{\mathbf{V}, \mathbf{\Omega}, \mathbf{u}_\infty, \mathbf{f}^e\right\} \Rightarrow \left\{-\mathbf{V}, -\mathbf{\Omega}, -\mathbf{u}_\infty, -\mathbf{f}^e\right\} \quad \longrightarrow \quad \{\mathbf{u}, p\} \Rightarrow \{-\mathbf{u}, -p\}$$

▶ Motion reversal of boundaries, external force density and ambient flow reverses sign of flow pattern only, but not its shape.



Highly viscous fluid

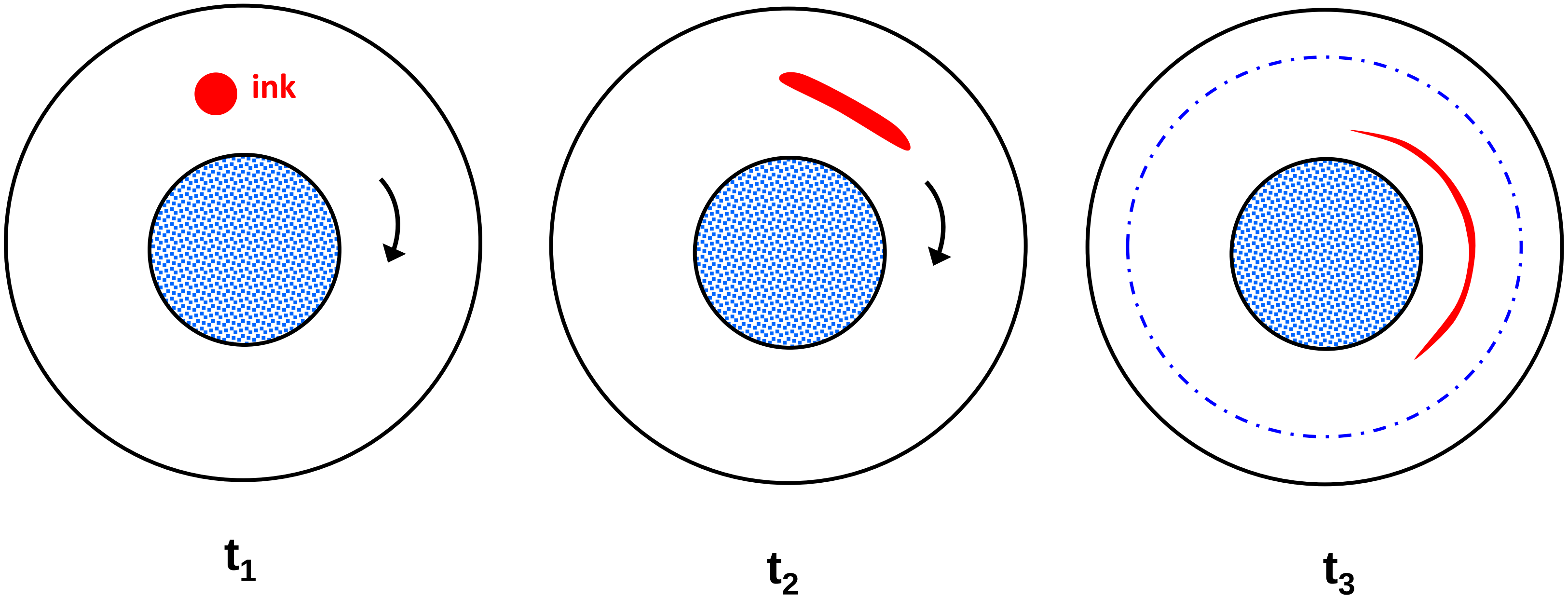


Low - viscosity fluid

- Laminar flow at Re << 1: kinematic reversibility and reciprocal history
- Rotation speed irrelevant

- Irreversible motion of dye across circular stream lines for Re > 1
- Diffusion causes cross-streamlines particle motion

G.I. Taylor, Cambridge



- **Particle motion across circular stream lines induced by:**

  - Brownian motion or external noise source

  - Inertia effects (Re ~ 1)

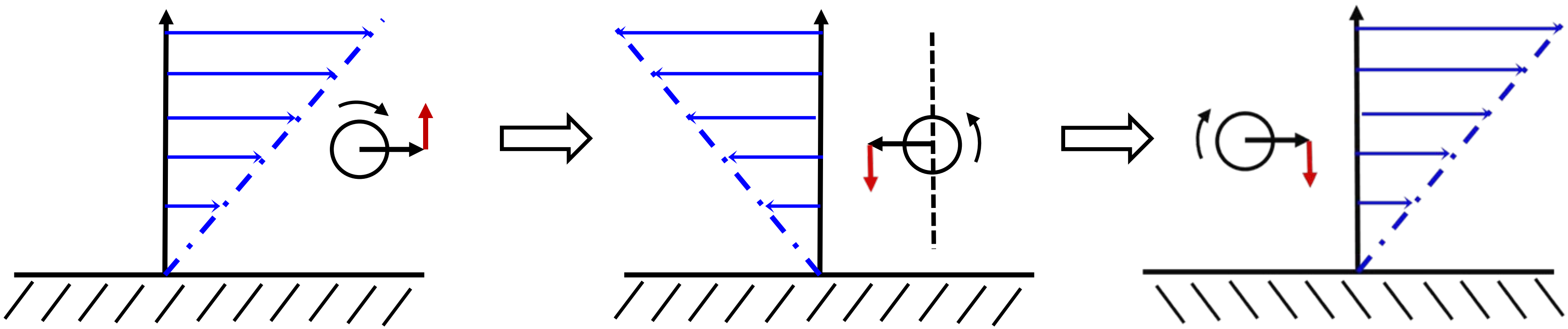
  - Many - particle HI in sufficiently dense systems (chaotic hydrodynamic motion)

  - Reversibility - breaking direct particle interactions such as surface roughness

D. Pine et al., Nature **438** (2005)
J. Gollub and D. Pine, Physics Today, August 2006

Application: motion in highly symmetric systems

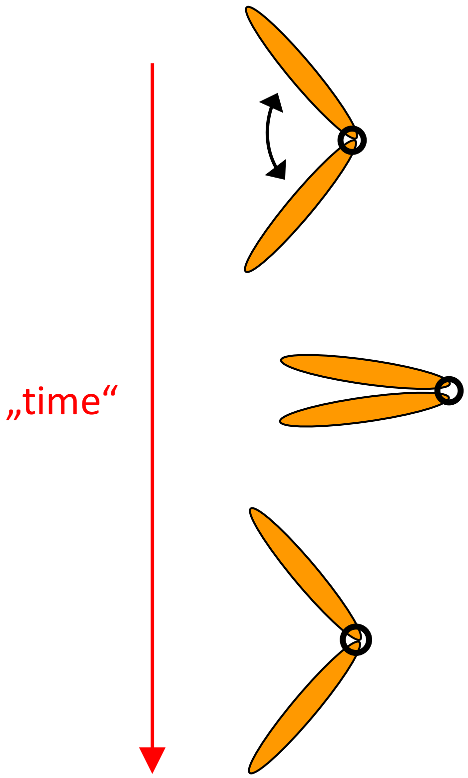
$\{\mathbf{u}_\infty, \mathbf{V}, \mathbf{\Omega}\}$ $\{-\mathbf{u}_\infty, -\mathbf{V}, -\mathbf{\Omega}\}$

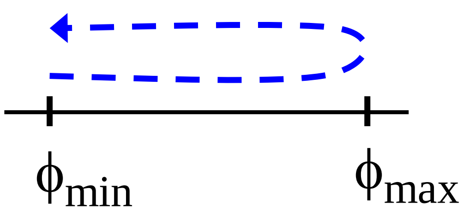


$$\Delta \mathbf{V} = 0$$

- Lift forces arise only when non- zero inertial contributions: $d\mathbf{u}/dt \neq 0$
- $\Delta \mathbf{V} \neq 0$ also for flexible particles (polymers, drops)

Purcell's scallop theorem for microswimmers





- **Internal forces and torques only:**

$$\mathbf{F}^{h} = 0 = -\mathbf{F}^{e} \qquad \mathbf{T}^{h} = 0 = -\mathbf{T}^{e}$$

- swimmers act as force dipoles in far – field flow

- **Purcell's scallop theorem:**

For net displacement after one shape cycle:

- non - reciprocal sequence of body deformations:
- at least 2 - parametric deformations (two hinges)
- skew – symmetric motion

E.M. Purcell, *Life at low Reynold's number*,
Am. J. Phys. **45**, 3 (1977)

- Non-reciprocal periodic motion is required: - **helical flagellum motion**

  - **two degrees of freedom for motion**

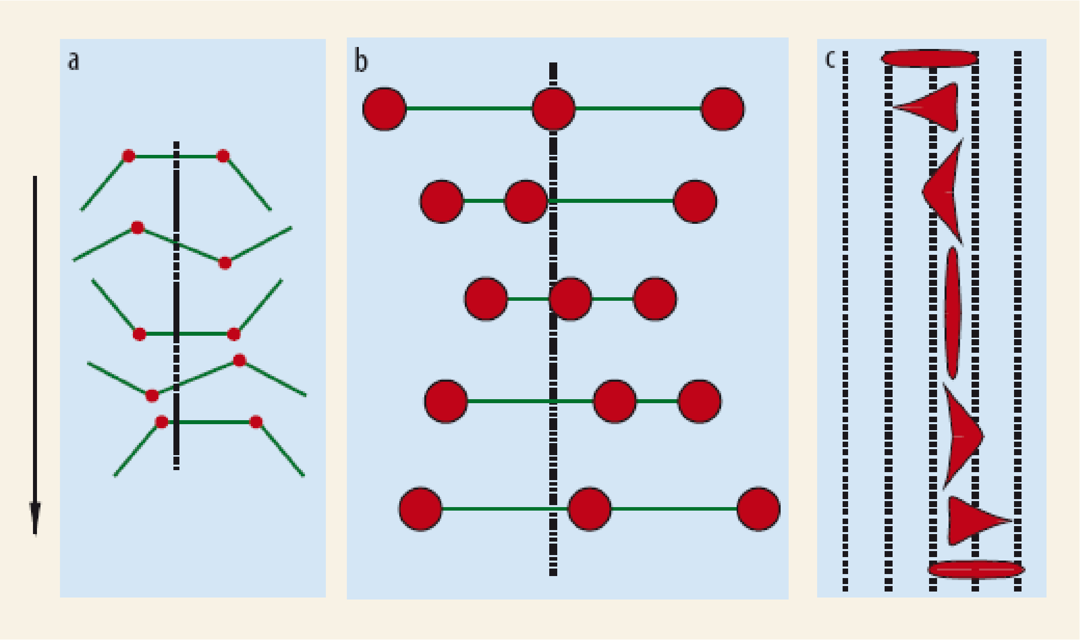
Re << 1: microrganism in water or macroscopic swimmer in glycerin

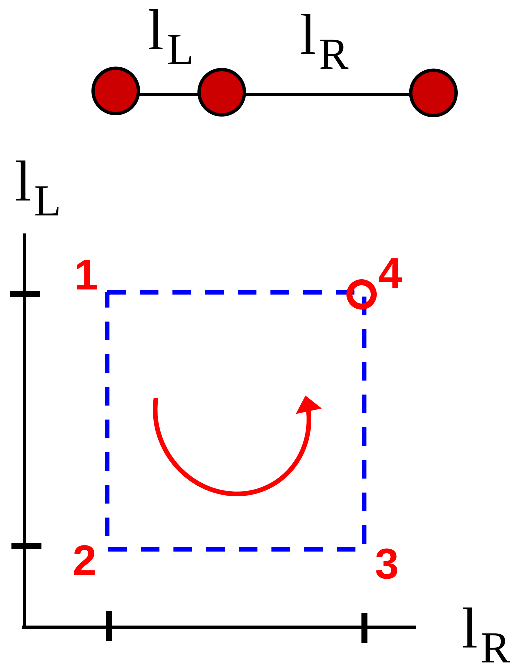
Simple artificial microswimmers

Purcell swimmer

3 - spheres swimmer

artificial amoeba





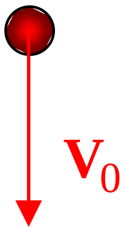
non-zero area swept out

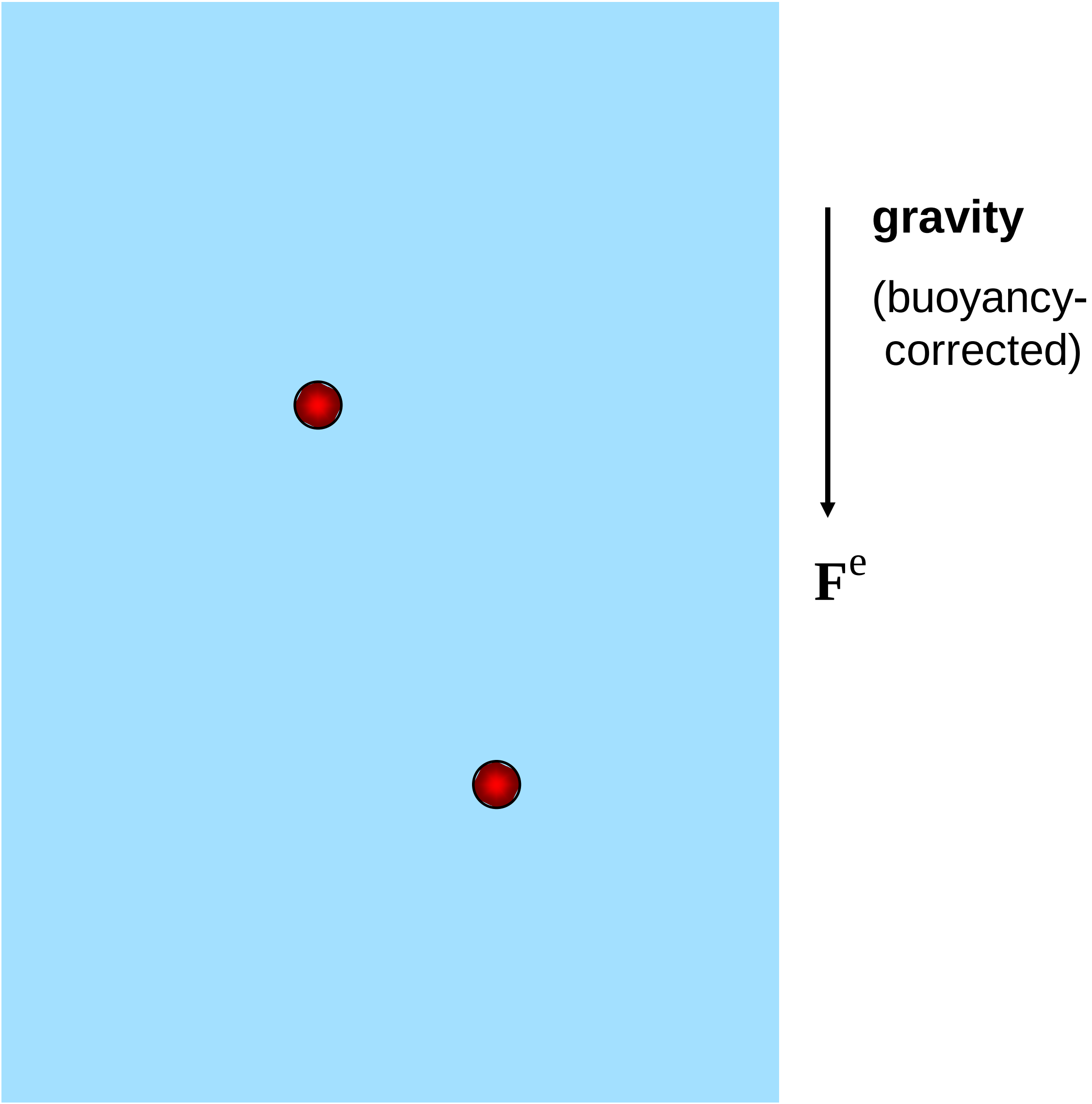
G. Nägele, ***Colloidal Hydrodynamics***, in Proceedings of the International School of Physics, "Enrico Fermi", Course 184 "Physics of Complex Colloids", ed. by C. Bechinger, F. Sciortino and P. Ziherl, (IOS, Amsterdam; SIF, Bologna) (2013)

Sedimentation of two non - Brownian Spheres (Re << 1)

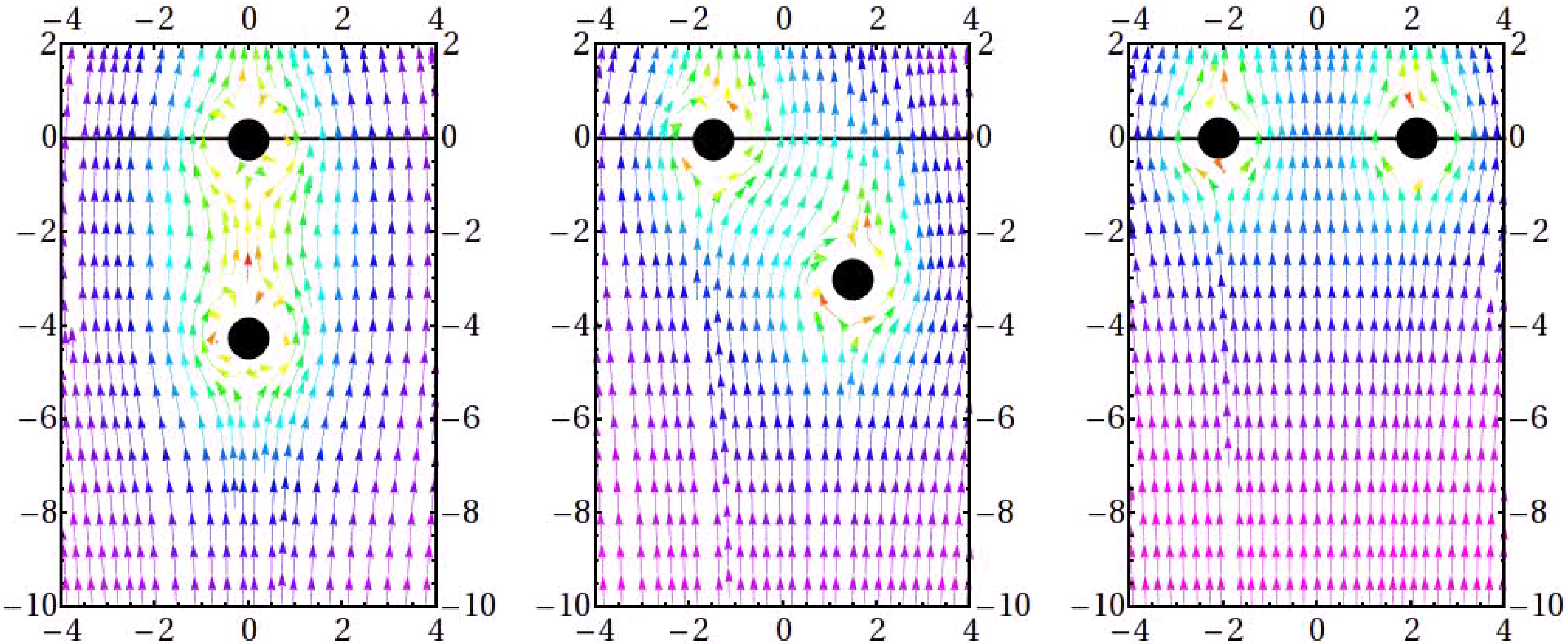
$$\mathbf{V}_0 = \mu_0 \mathbf{F}^e$$

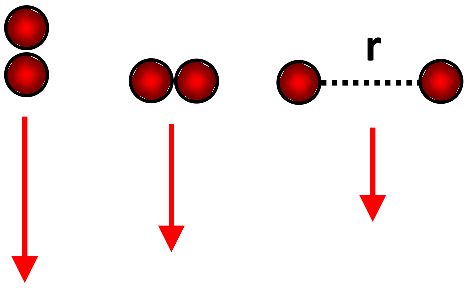
$$\mu_0^t = \frac{1}{6\pi\eta_0 a}$$





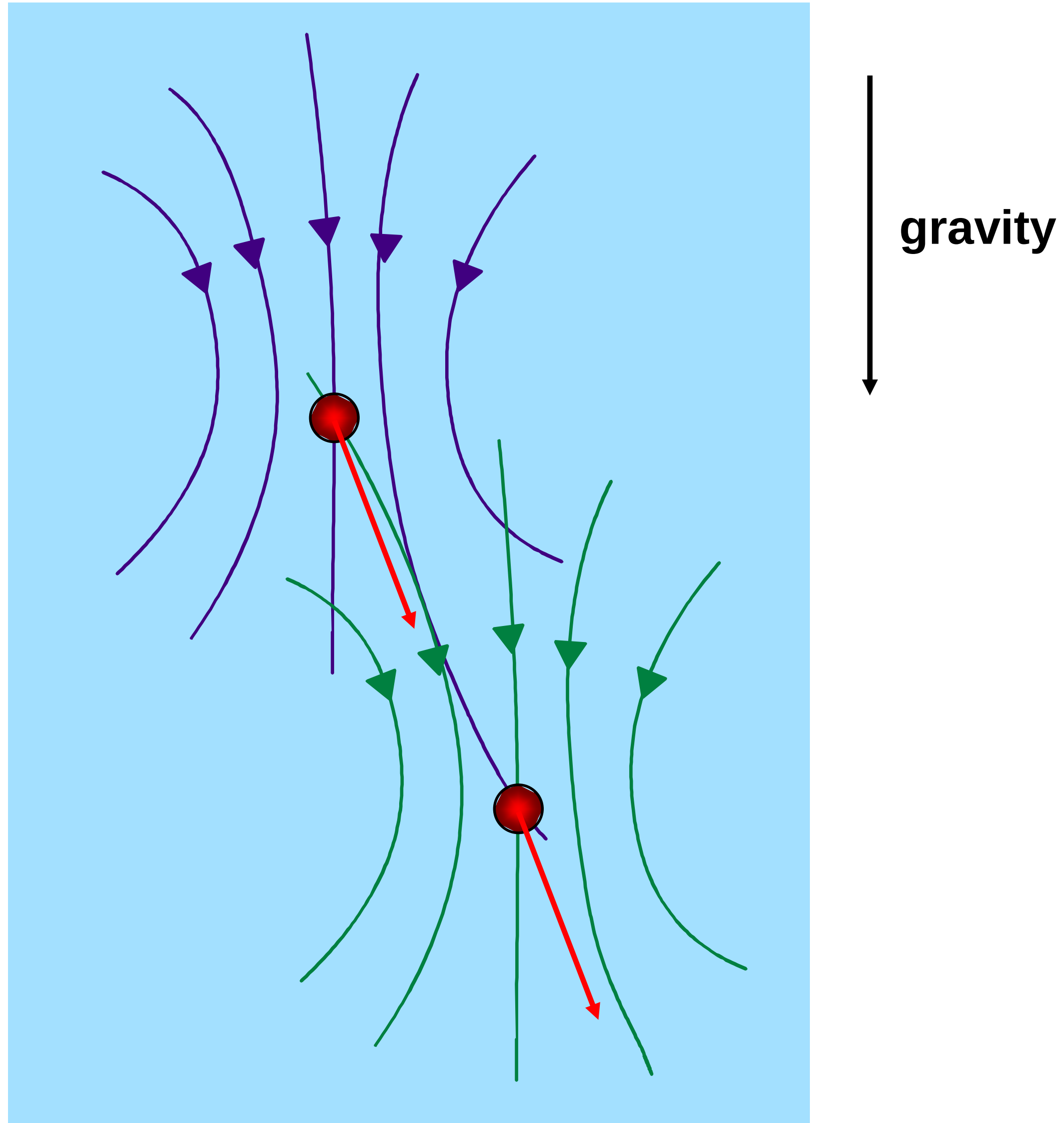
The sedimentation race: bet which pair settles fastest, and how ?

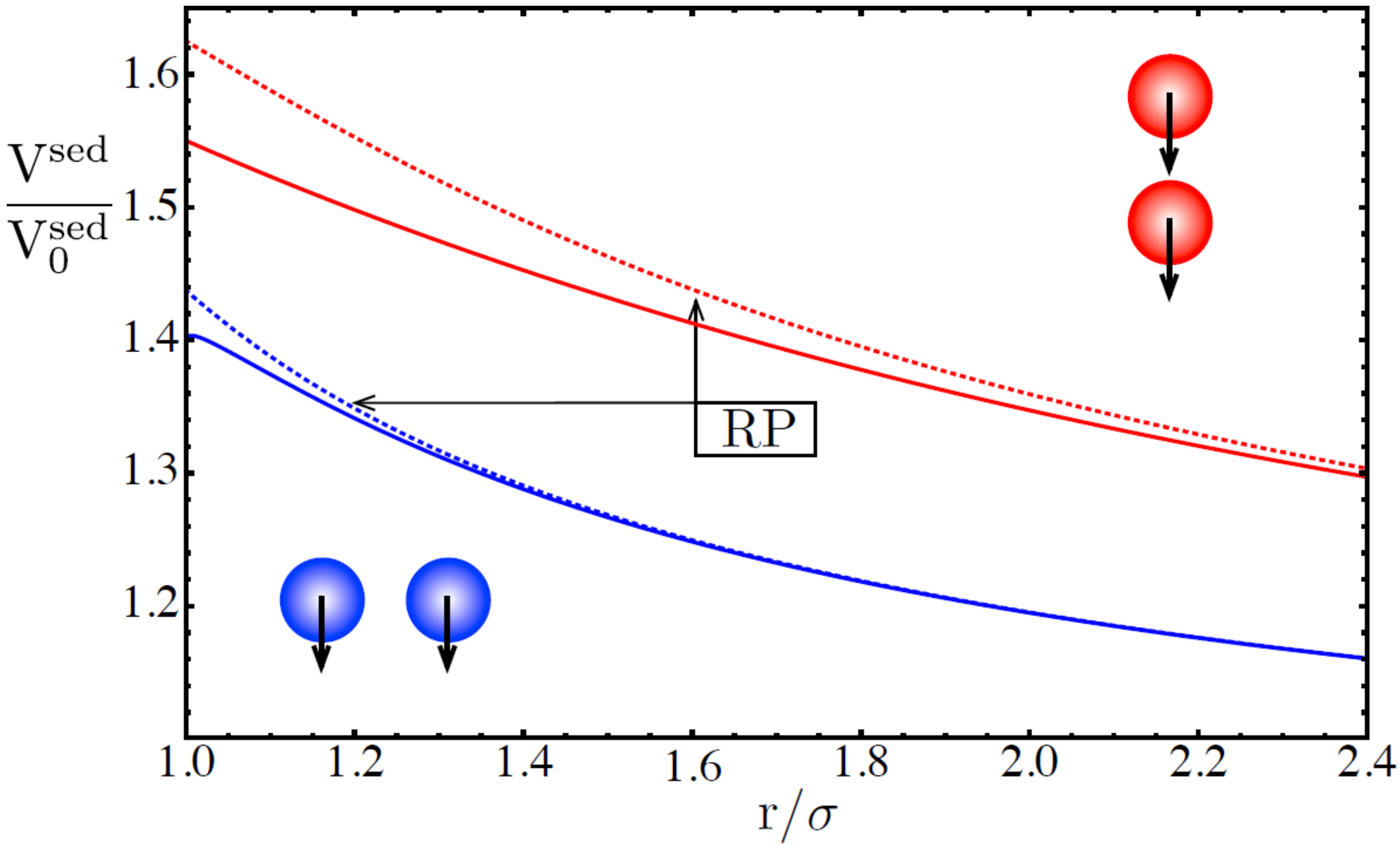




constant sep. vector **r**

$$V_{\mathrm{sed}}^{\mathrm{pair}} > V_{\mathrm{sed}}^{0} = \mu_0^{t}\, \mathbf{F}^{e}$$

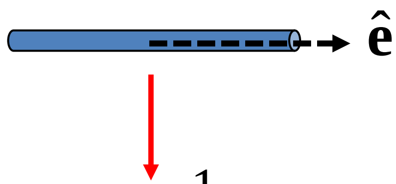




- Drag - along effect strongest for in - line sedimentation
- Lubrication plays no role for motions considered here (**Rotne – Prager o.k. for r > 5a**)

Sedimentation of a non - Brownian rod (Re << 1)

$$\mathbf{V} = \boldsymbol{\mu} \cdot \mathbf{F}^e$$



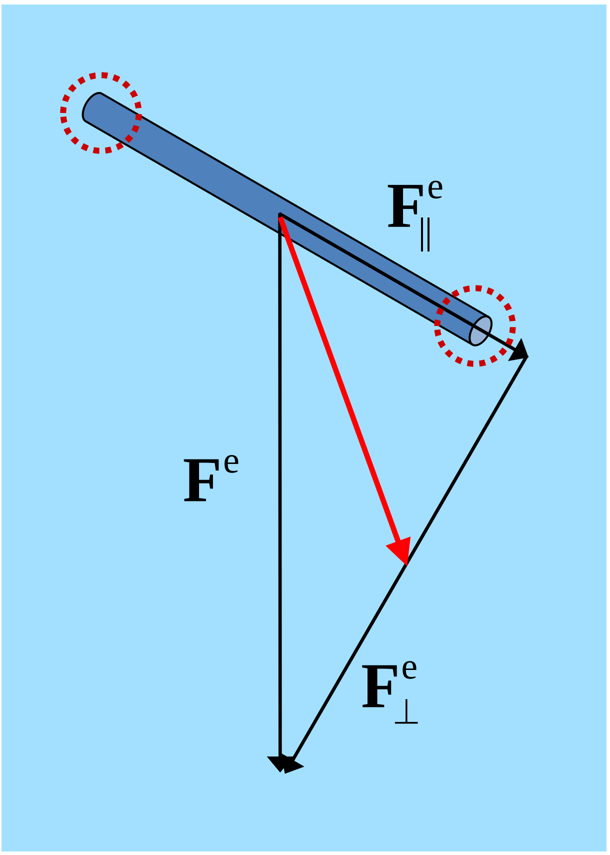
$$\mu_\perp \approx \frac{1}{2}\mu_{||}$$

(transl. mobilities for L >> D)

$$\boldsymbol{\mu} = \mu_{||}\hat{\mathbf{e}}\hat{\mathbf{e}} + \mu_\perp\left(\mathbf{1} - \hat{\mathbf{e}}\hat{\mathbf{e}}\right)$$

$$\mathbf{V} = \mu_{||}\mathbf{F}^e{}_{||} + \mu_\perp\mathbf{F}^e{}_\perp$$

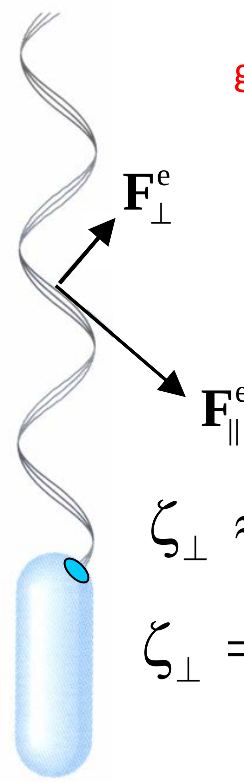
$$\left(\hat{\mathbf{e}}\,\hat{\mathbf{e}}\right)_{\alpha\beta} = \hat{e}_\alpha\,\hat{e}_\beta$$



Experiment: needle in syrup
no rotation

$$\mathbf{F}^e = \zeta \cdot \mathbf{V}$$

given



$$\zeta_\perp \approx 2\,\zeta_{||}$$

$$\zeta_\perp = 1/\mu_\perp$$

Flagella bundle:
HI synchronized

Apparent like - charge attraction of particles near boundary

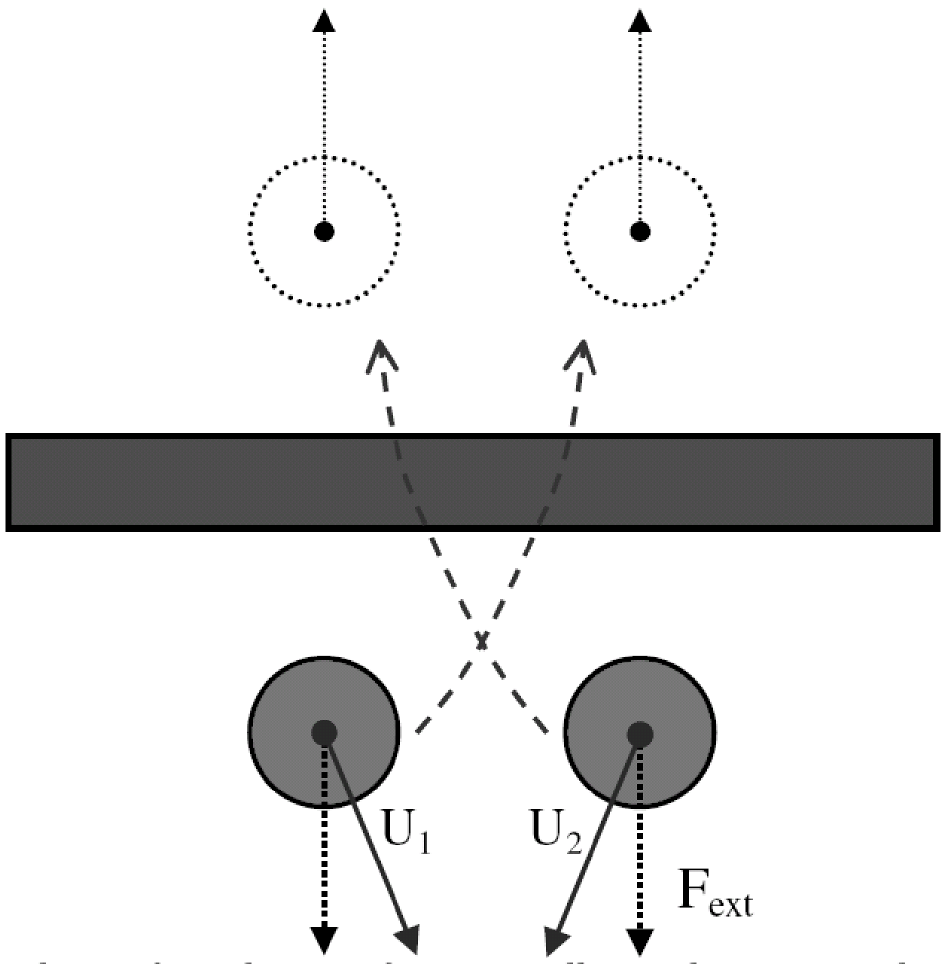


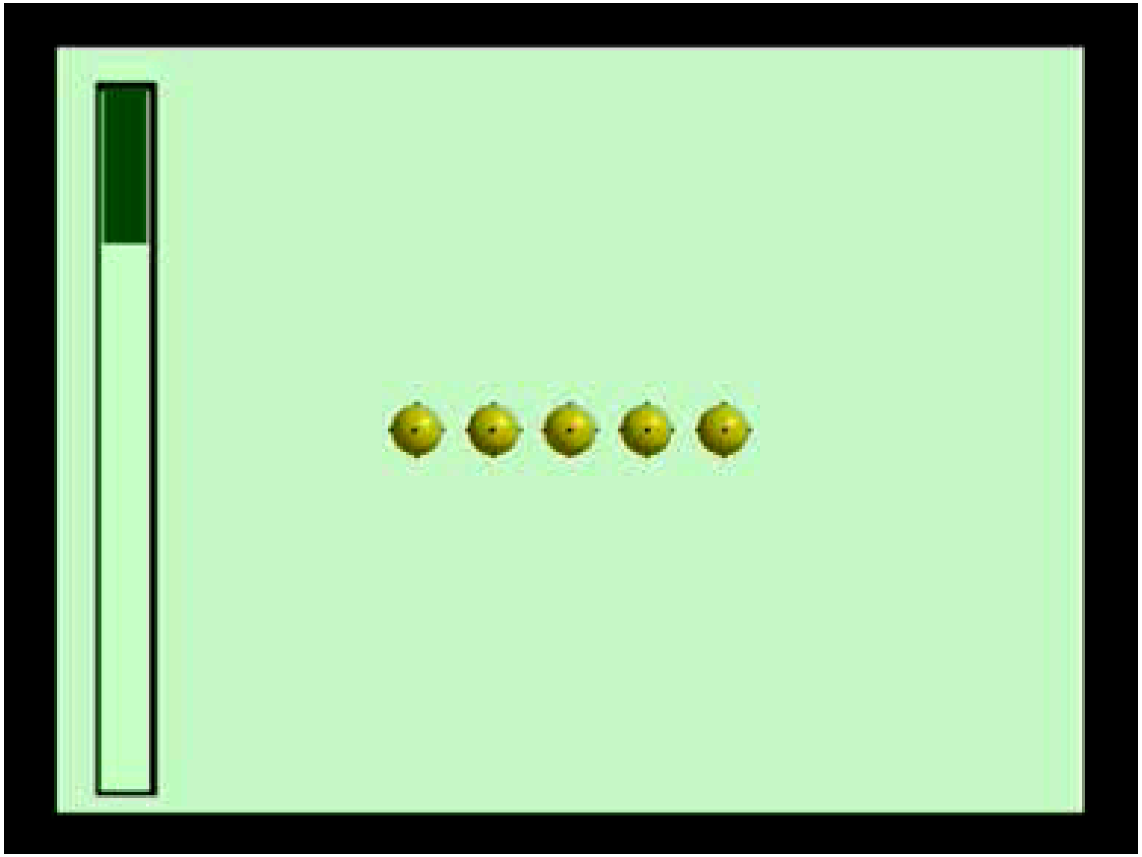
figure taken from:
Squires & Brenner, PRL (2000)

charged glass wall or
liquid - air interface

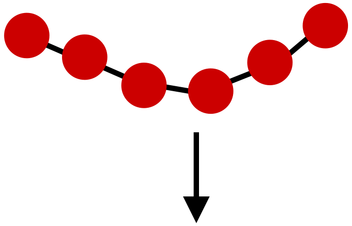
$F_{ext} \rightarrow - F_{ext}$?

- Attractive wall: apparent repulsion

Five non - Brownian spheres in equidistant start configuration

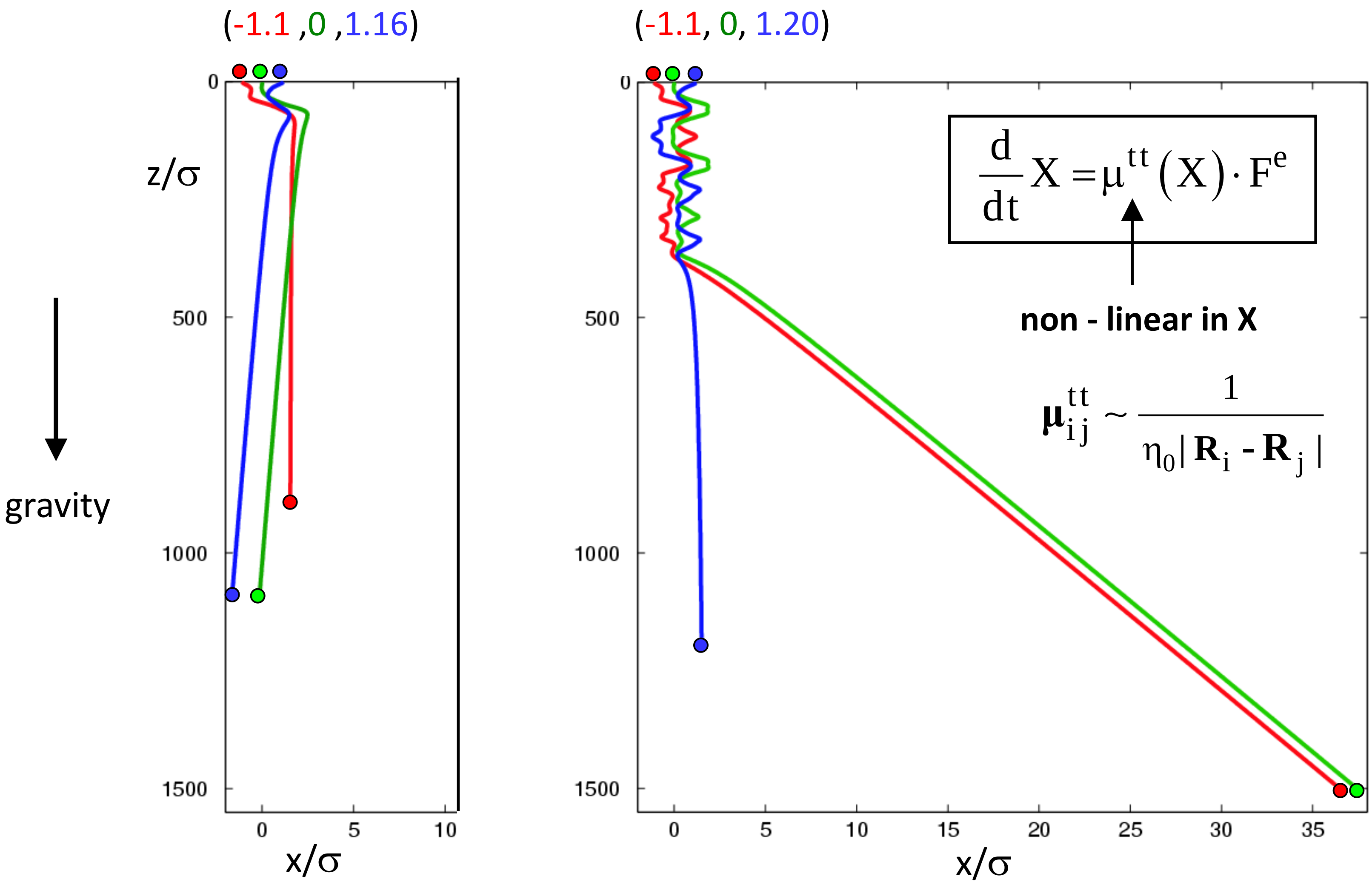


- pair distances are varying
- dimer formation: „kissing“
- sensitive dependence on initial conditions
- end - lagging of polymers



Simulation by: G. Kneller, Centre de Biophysique Moleculaire, Orleans

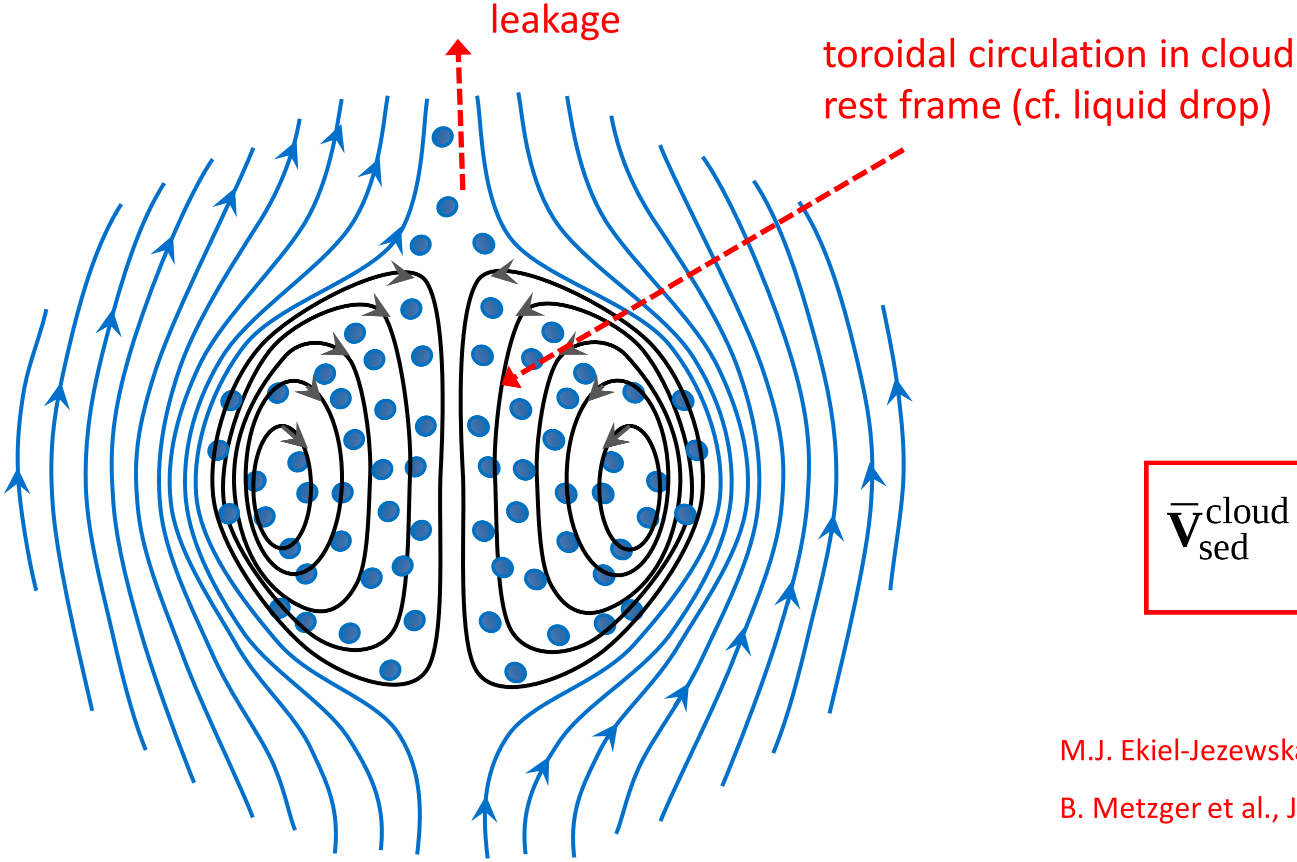
Three sedimenting non - Brownian Spheres: non - symmetric start configuration

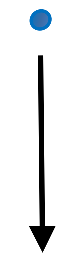


- Sensitive dependence on initial configuration for N > 2 $\rightarrow$ **chaotic trajectories**

Courtesy: M. Ekiel-Jezewska & E. Wajnryb, Phys. Rev. E **83**, 067301 (2011)

Sedimentation: spherical cloud of non - Brownian particles (radius R)





$$\mathbf{V}_{\text{sed}}^{0} = \mu_{0}^{t}\,\mathbf{F}^{e}$$

$$\bar{\mathbf{V}}_{\text{sed}}^{\text{cloud}} \approx \mathbf{V}_{\text{sed}}^{0} + \frac{N-1}{5\pi\eta_0 R}\,\mathbf{F}^{e}$$

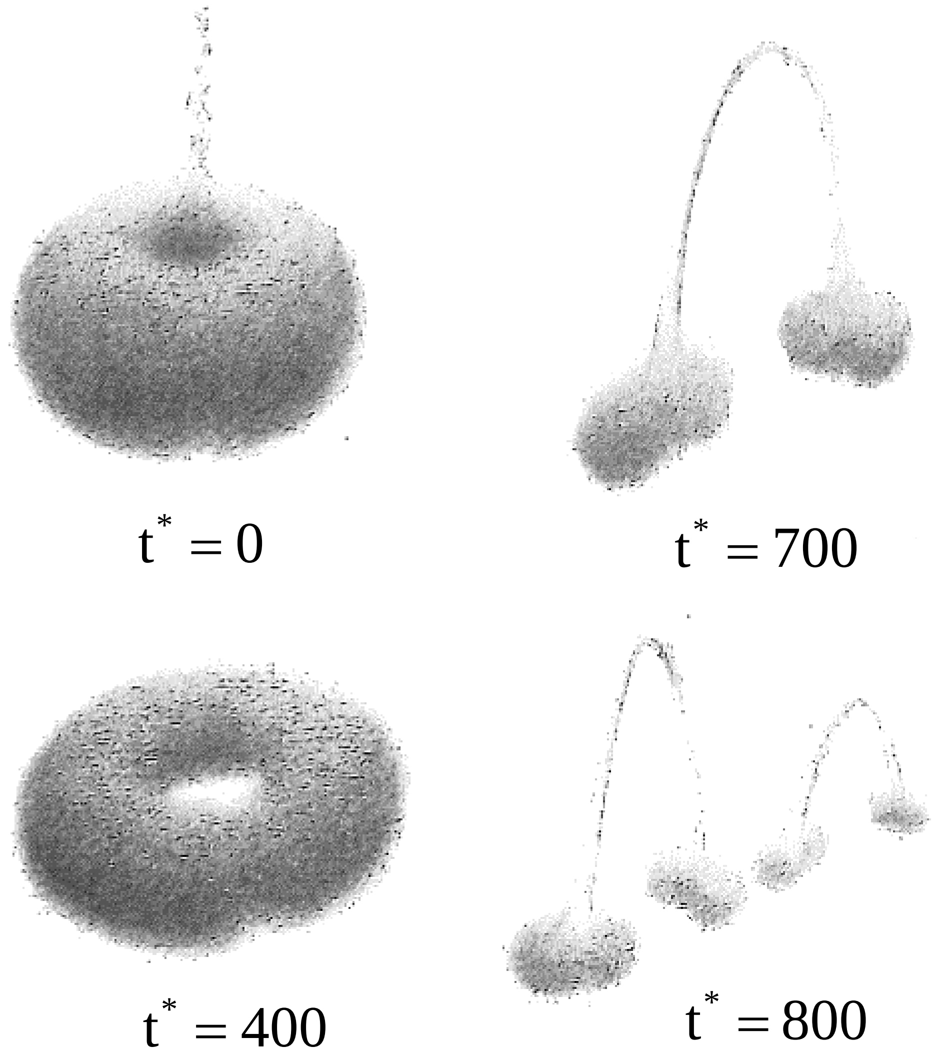
M.J. Ekiel-Jezewska, Phys. Fluids **18** (2006),

B. Metzger et al., J. Fluid Mech. **580,** 238 (2007)

- Cloud sediments faster than single bead
- Instability for large N and large settling time (chaotic fluctuations due to many-bead HI)

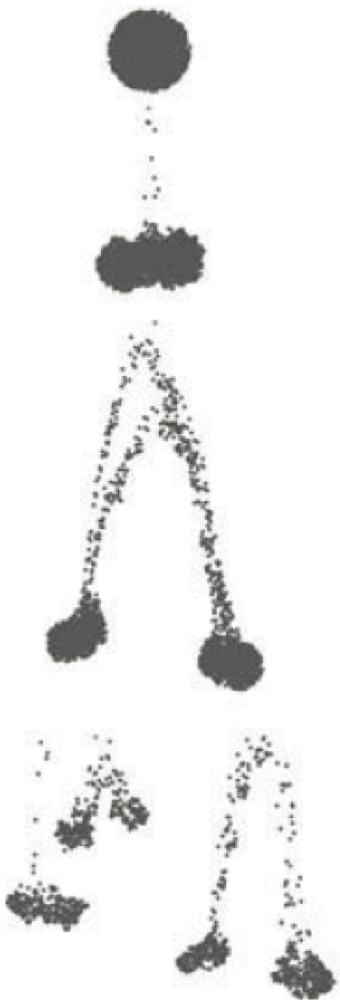
- Evolution: spherical cloud → torus → breakup in two clouds → …

$$t^* = t / \tau_R^{sed}$$

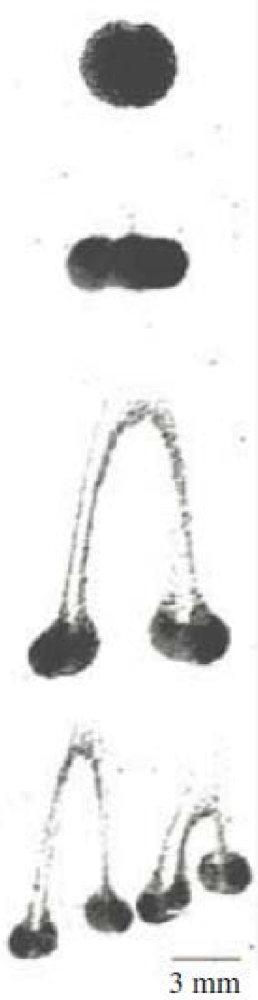


taken from: E. Guazzelli and J.F. Morris, *A Physical Introduction to Suspension Dynamics*, Cambridge Univ. Press (2012)

- Point - particle simulation
  (N = 3000)



- Glass spheres (a ≈ 70 μm)
  (in silicon oil)



taken from: B. Metzger, M. Nicolas and E. Guazzelli, J. Fluid Mech. **580,** 238 (2007)

2. Low-Reynolds number flow

- Colloidal time scales
- Stokes equation
- Point force solution
- Boundary layer method
- Faxén laws for spheres

2.1 Colloidal time scales

$$\rho_f \left[\frac{\partial \mathbf{u}(\mathbf{r},t)}{\partial t} + \mathbf{u}(\mathbf{r},t)\cdot\nabla\mathbf{u}(\mathbf{r},t) \right] = -\nabla p(\mathbf{r},t) + \eta_0 \nabla^2 \mathbf{u}(\mathbf{r},t) + \mathbf{f}^e(\mathbf{r},t)$$

Navier - Stokes Eq.
incompressible flow

$$\nabla \cdot \mathbf{u}(\mathbf{r},t) = 0$$

$$\Delta t \gg \tau_{sound} = a / c_{sound} \sim 10^{-10} \text{ sec}$$

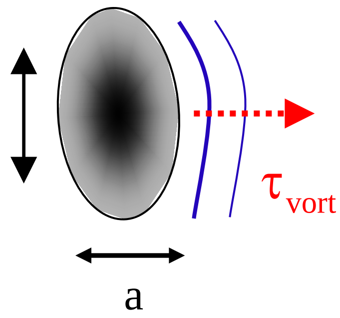
volumetric force density **on** fluid by external fields

$$Re = \frac{\text{inertial force}}{\text{viscous force}} = \frac{\rho_f V_p^2 / a}{\eta_0 V_p / a^2} = \frac{\rho_f a V_p}{\eta_0} \ll 1$$

(particle) Reynolds number

$$\rho_f \frac{\partial \mathbf{u}(\mathbf{r},t)}{\partial t} = -\nabla p(\mathbf{r},t) + \eta_0 \nabla^2 \mathbf{u}(\mathbf{r},t) + \mathbf{f}^e(\mathbf{r},t)$$

still includes vorticity diffusion



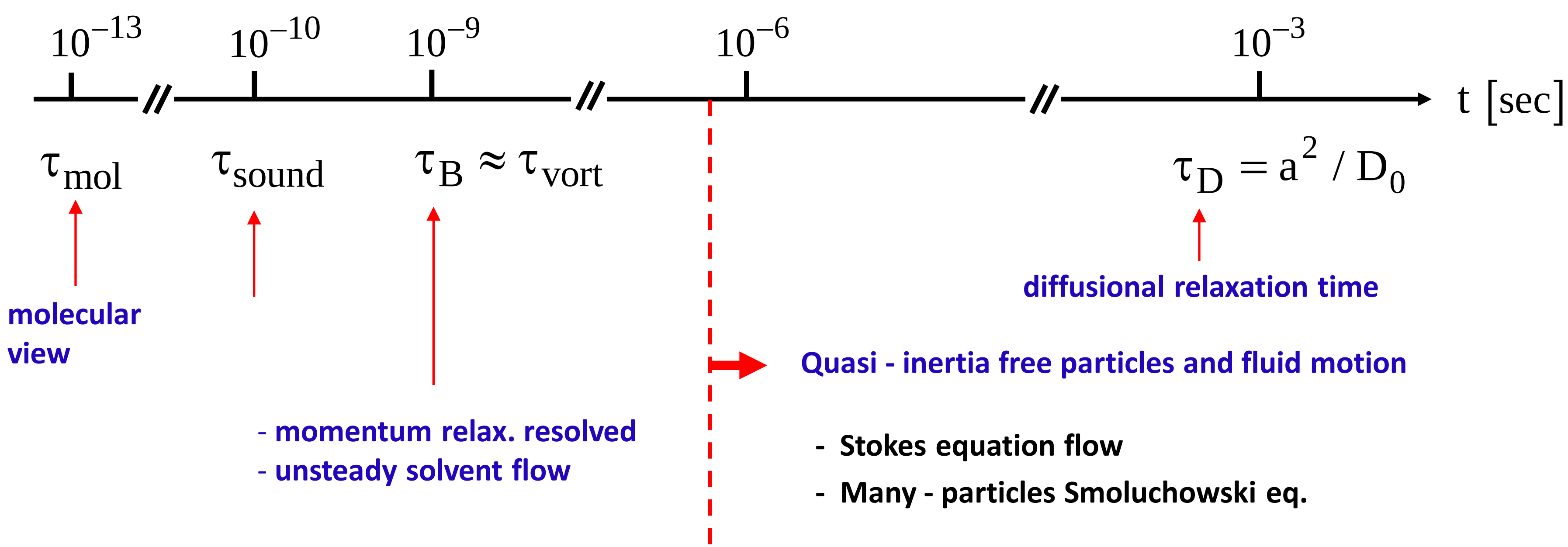
$$\Delta t \gg \tau_{vort} = \frac{a^2 \rho_f}{\eta_0} \sim 10^{-9} \text{ sec} \quad \Longrightarrow \quad \frac{\rho_f V_p / \Delta t}{\eta_0 V_P / a^2} \ll 1$$

$$-\nabla p(\mathbf{r}) + \eta_0 \nabla^2 \mathbf{u}(\mathbf{r}) + \mathbf{f}^e(\mathbf{r}) = 0$$

Stokes equation

Inertia - free force balance

Overview: time scales (particles with a = 100 nm in water)



momentum relax. time

$$\tau_B = \frac{M}{\zeta_0} = \frac{2}{9}\left(\frac{\rho_p}{\rho_f}\right)\tau_{vort}$$

Stokes #

$$St = \frac{\tau_B}{\tau_{ext}} = \frac{2}{9}\left(\frac{\rho_p}{\rho_f}\right)Re$$

Advection time

$$\tau_{ext} = \frac{a}{V_p}$$

- **Colloids and microswimmer:** Re <<1 and St << 1
- Dry powder granular dynamics: St >>1 (large & heavy particles in a gas)

2.2 Stokes equation

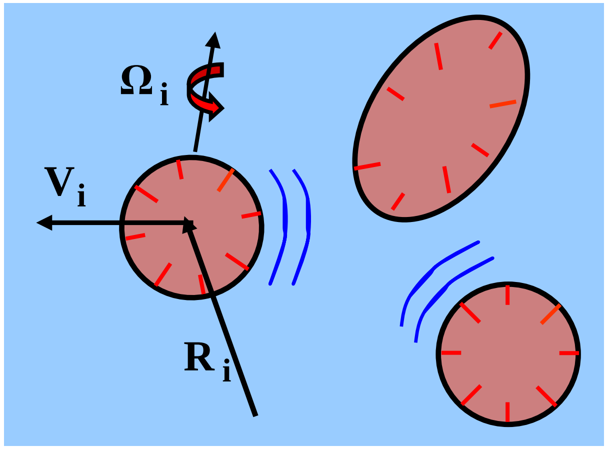
- Linear Stokes equation BVP for N rigid particles in infinite and unbounded fluid (no ext. forces)

$$-\nabla p(\mathbf{r}) + \eta_0 \nabla^2 \mathbf{u}(\mathbf{r}) = \mathbf{0}$$

zero total force $(\mathbf{r} \in V_{fluid})$

$$\nabla \cdot \mathbf{u}(\mathbf{r}) = 0$$

fluid incompressibility



$$\mathbf{u}(\mathbf{r}) = \mathbf{V}_i + \boldsymbol{\Omega}_i \times (\mathbf{r} - \mathbf{R}_i)$$

for **r** on particle surface S_i (stick inner BC)

Quiescent fluid	Ambient flow
$\mathbf{u}(\mathbf{r}) \to 0\,,\ \lvert\mathbf{r}\rvert \to \infty$	$\mathbf{u}(\mathbf{r}) \to \mathbf{u}_\infty(\mathbf{r})\,,\ \lvert\mathbf{r}\rvert \to \infty$
$p(\mathbf{r}) \to \text{const}\,,\ \lvert\mathbf{r}\rvert \to \infty$	$p(\mathbf{r}) \to p_\infty(\mathbf{r})\,,\ \lvert\mathbf{r}\rvert \to \infty$
outer BC for **quiescent** fluid	**ambient** flow due to sources „at infinity“

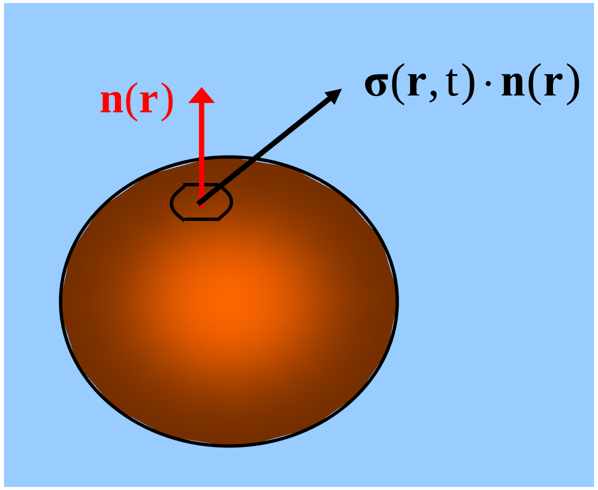
Helmholtz (1868) :

- Unique solution **u**(**r**) for given BC‘s on inner and outer fluid boundaries
- Of all **u**(**r**) with div **u**(**r**) = 0, Stokes flow has minimal dissipation

$$0 = -\nabla p(\mathbf{r}) + \eta_0 \nabla^2 \mathbf{u}(\mathbf{r}) = \nabla \cdot \boldsymbol{\sigma}^h(\mathbf{r})$$

$$\boldsymbol{\sigma}^h(\mathbf{r}) = -p(\mathbf{r})\mathbf{1} + \eta_0 \left[\nabla \mathbf{u} + (\nabla \mathbf{u})^T \right]$$

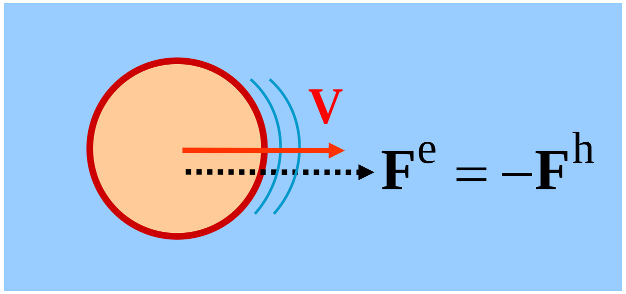
fluid stress tensor



$$\sigma^h_{\alpha\beta}(\mathbf{r}) = -p(\mathbf{r})\,\delta_{\alpha\beta} + \eta_0 \left[\partial_\alpha u_\beta(\mathbf{r}) + \partial_\beta u_\alpha(\mathbf{r}) \right]$$

$$\mathbf{F}^h = \int_{S^+} dS\, \underbrace{\boldsymbol{\sigma}^h(\mathbf{r};X) \cdot \mathbf{n}(\mathbf{r})} = -\mathbf{F}^e$$

fluid force / area on sphere surface element dS
at **r** exerted by surrounding fluid layer



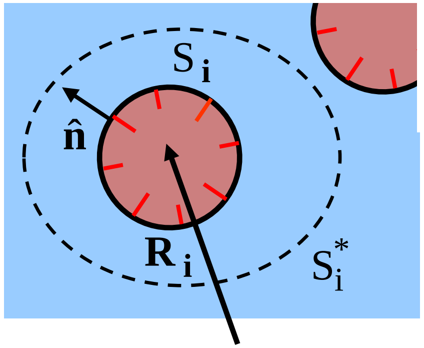
single sphere force balance

Mobility and friction matrices

- Hydrodynamic force and torque **on** surface of particle i

$$\mathbf{F}_i^h = \int_{S_i^+} dS\, \boldsymbol{\sigma}^h(\mathbf{r};X)\cdot\mathbf{n}(\mathbf{r}) = \int_{S_i^*} dS\, \boldsymbol{\sigma}^h(\mathbf{r};X)\cdot\mathbf{n}(\mathbf{r}) = -\mathbf{F}_i^e$$

$$\mathbf{T}_i^h = \int_{S_i^+} dS\,(\mathbf{r}-\mathbf{R}_i)\times\boldsymbol{\sigma}^h(\mathbf{r};X)\cdot\mathbf{n}(\mathbf{r}) = -\mathbf{T}_i^e$$



$$\nabla\cdot\boldsymbol{\sigma}^h = \mathbf{0} \quad (\mathbf{r}\in V_{fl})$$

2.3 Point-force solution (Oseen)

- Find solution of Stokes eq. for a point force **F** acting on quiescent & unbound fluid at **r** :

$$-\nabla p(\mathbf{r}) + \eta_0 \nabla^2 \mathbf{u}(\mathbf{r}) = -\mathbf{f}(\mathbf{r}) \qquad \nabla \cdot \mathbf{u}(\mathbf{r}) = 0 \qquad \mathbf{f}(\mathbf{r}) = \mathbf{F}\,\delta(\mathbf{r}-\mathbf{0})$$

volumetric force density on fluid

- The solution for outer BC **u**(**r** $\to \infty$) = 0 and p(**r** $\to \infty$) = 0 is :

$$p(\mathbf{r}) = \mathbf{Q}_0(\mathbf{r}) \cdot \mathbf{F} \qquad \mathbf{Q}_0(\mathbf{r}) = \frac{1}{4\pi r^2}\hat{\mathbf{r}}$$

$$\mathbf{u}(\mathbf{r}) = \mathbf{T}_0(\mathbf{r}) \cdot \mathbf{F} \qquad \mathbf{T}_0(\mathbf{r}) = \frac{1}{8\pi\eta_0 r}\left(\mathbf{1} + \hat{\mathbf{r}}\hat{\mathbf{r}}\right)$$

Oseen tensor

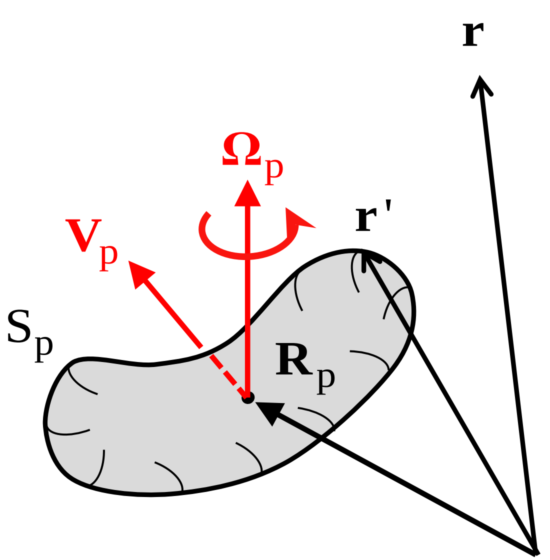
$$(\mathbf{T}_0)_{\alpha\beta}(\mathbf{r}) = \frac{1}{8\pi\eta_0 r}\left(\delta_{\alpha\beta} + \frac{x_\alpha x_\beta}{r^2}\right)$$

$$\nabla \cdot \mathbf{u}(\mathbf{r}) = 0 \Rightarrow \nabla \cdot \mathbf{T}_0(\mathbf{r}) = 0$$ including **r** = 0

$$\mathbf{u}(\mathbf{r}) = \int d\mathbf{r}'\,\mathbf{T}_0(\mathbf{r}-\mathbf{r}') \cdot \mathbf{f}(\mathbf{r}')$$

Boundary layer method

$$\mathbf{u}(\mathbf{r}) = \int d\mathbf{r}'\mathbf{T}_0(\mathbf{r}-\mathbf{r}')\cdot\mathbf{f}^e(\mathbf{r}')$$ zero ambient flow



- **Rigid** particle p of arbitrary shape with **stick** (no-slip) BC:

$$\mathbf{u}_D(\mathbf{r}) \equiv \mathbf{u}(\mathbf{r}) - \mathbf{u}_\infty(\mathbf{r}) = \int_{S_p} dS'\,\mathbf{T}_0(\mathbf{r}-\mathbf{r}')\cdot\mathbf{f}^{(s)}(\mathbf{r}')$$

disturbance flow

single - layer „potential“

$$\mathbf{f}^{(s)}(\mathbf{r}') = -\boldsymbol{\sigma}^h(\mathbf{r}')\cdot\mathbf{n}(\mathbf{r}')$$ Surface traction on fluid at surface point **r‘**

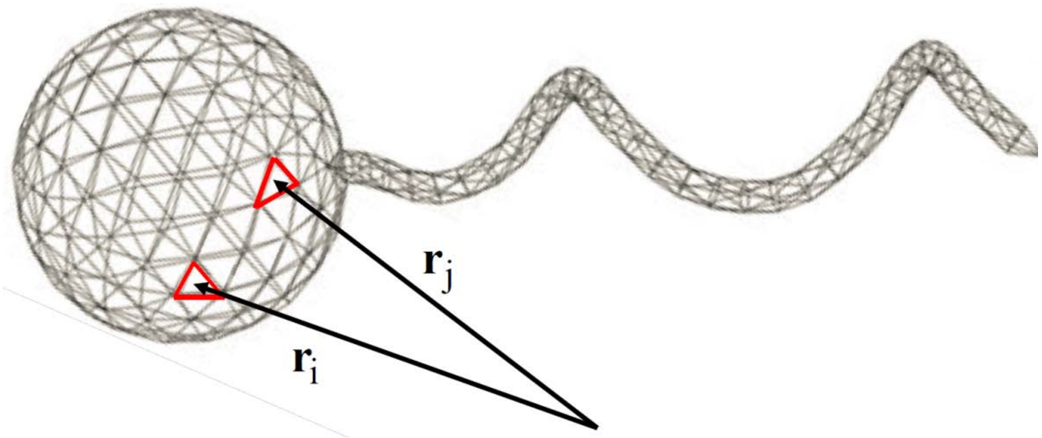
- Insertion of no - slip BC ⇨ t wo-dimensional integral equation for traction:

$$\mathbf{V}_p + \boldsymbol{\Omega}_p \times \left(\mathbf{r}-\mathbf{R}_p\right) - \mathbf{u}_\infty(\mathbf{r}) = \int_{S_p} dS'\,\mathbf{T}_0(\mathbf{r}-\mathbf{r}')\cdot\mathbf{f}^{(s)}(\mathbf{r}') \qquad (\mathbf{r}\in S_p)$$

$$\{\mathbf{V}_p, \mathbf{\Omega}_p, \mathbf{u}_\infty\} \Rightarrow \{\mathbf{f}^{(s)}(\mathbf{r}')\} \Rightarrow \{\mathbf{F}_p^h, \mathbf{T}_p^h, \mathbf{u}\}$$

- Particle with complex shape: Discretization / Triangularization

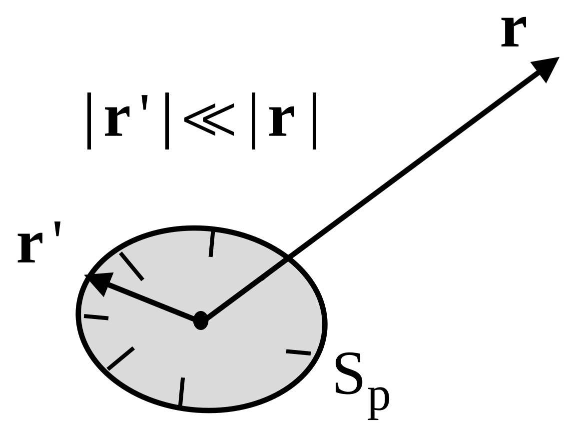
$$\mathbf{V}_p + \mathbf{\Omega}_p \times (\mathbf{r}_i - \mathbf{R}_p) - \mathbf{u}_\infty(\mathbf{r}_i) = \sum_{j=1}^{N} \underbrace{\mathbf{T}_0(\mathbf{r}_i - \mathbf{r}_j)}_{3N\times 3N \text{ inversion}} \cdot \mathbf{f}^{(s)}(\mathbf{r}_j) \qquad (i \in \{1,\ldots,N\})$$



- Frequently only relations $\{V_p, \Omega_p\} \Leftrightarrow \{F_p^H, \Omega_p^H\}$ are required

- „Rapid prototypeing“:
  form complex shapes (proteins) by connecting spherical beads

Far – distance flow field around a neutral particle



- Expand around point inside particle:

$$\mathbf{u}_D(\mathbf{r}) = \int_{S_p} dS' \left[\mathbf{T}_0(\mathbf{r}) - \mathbf{r}'\cdot\nabla\mathbf{T}_0(\mathbf{r}) - \ldots\right]\cdot\mathbf{f}^{(s)}(\mathbf{r}')$$

- Split in symmetric and anti-symmetric parts:

$$\mathbf{u}_D(\mathbf{r}) \approx -\mathbf{T}_0(\mathbf{r})\cdot\mathbf{F}^h + \frac{1}{8\pi\eta_0 r^2}\hat{\mathbf{r}}\times\mathbf{T}^h - \frac{1}{8\pi\eta_0 r^2}\left(\hat{\mathbf{r}}\mathbf{1} - 3\hat{\mathbf{r}}\hat{\mathbf{r}}\hat{\mathbf{r}}\right):\mathbf{S}^h$$

- Freely mobile particle (force- and torque-free): $\mathbf{F}^h = 0 = \mathbf{T}^h$ **active microswimmer**

- Freely mobile particle creates O(r^{-2}) flow disturbance by its **symmetric force dipole**

$$\mathbf{S}^h = -\frac{1}{2}\int_{S_p} dS' \left[\mathbf{f}^{(s)}(\mathbf{r}')\mathbf{r}' + \mathbf{r}'\mathbf{f}^{(s)}(\mathbf{r}') - \frac{2}{3}\mathbf{1}\,\mathrm{Tr}\left(\mathbf{r}'\mathbf{f}^{(s)}(\mathbf{r}')\right)\right]$$

- rigid
- no - slip

Example: symmetric force dipole in y - direction (pusher: p > 0)

$$\mathbf{u}(\mathbf{r}) = \left[\mathbf{T}_0(\mathbf{r} - \frac{d}{2}\hat{\mathbf{y}}) - \mathbf{T}_0(\mathbf{r} + \frac{d}{2}\hat{\mathbf{y}}) \right] \cdot F^e \, \hat{\mathbf{y}}$$

$$\mathbf{S}^h = p\left(\hat{\mathbf{y}}\,\hat{\mathbf{y}} - \frac{1}{3}\mathbf{1} \right)$$

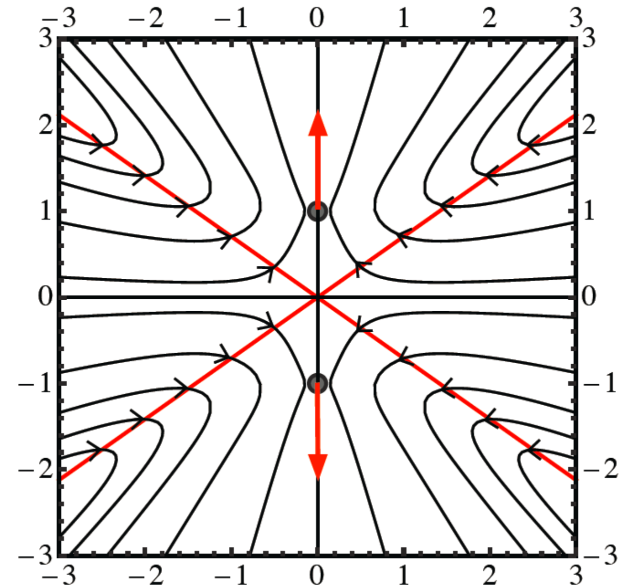
$$p = F^e \, d$$

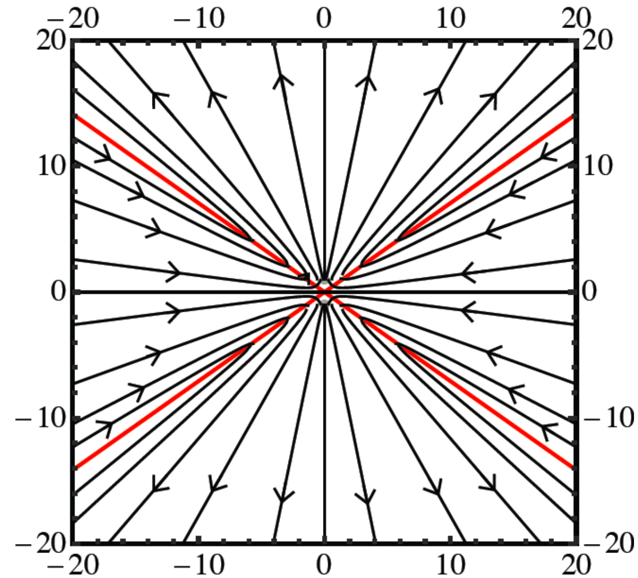
dipole moment

- Far – field flow : $\cos\theta = \hat{\mathbf{y}} \cdot \hat{\mathbf{r}}$

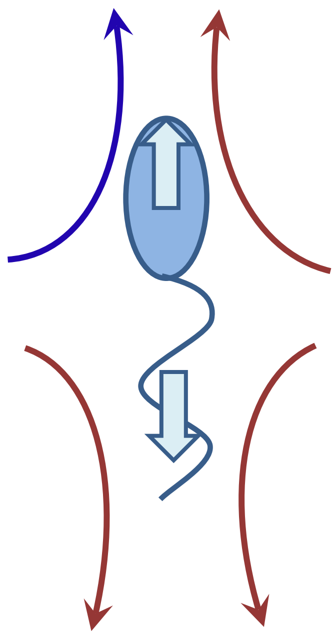
$$\mathbf{u}(\mathbf{r}) \sim \frac{p}{8\pi\eta_0 \, r^2}\left[3\cos^2\theta - 1 \right] \hat{\mathbf{r}}$$

- Swimmer describeable as static force dipole for distances >> d , and when time – averaged over strokes (non-reciprocal cycle, friction-asymmetric)

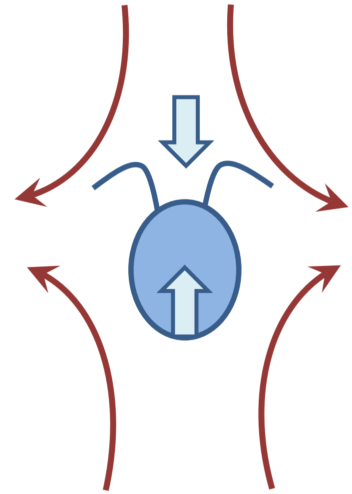


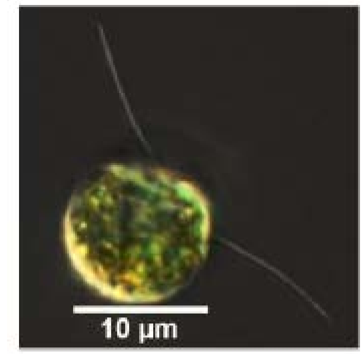


- **Pusher: $p > 0$**



- **Puller: $p < 0$**





Production stroke

- E. Coli, **salmonella**, sperm, …
- Propelling part at rear
- Tend to attract each other.

- **Algae Chlamydomonas**, …
- Propelling part on head side
- Tend to repel each other („asocial“).

2. 4 Faxén laws for spheres

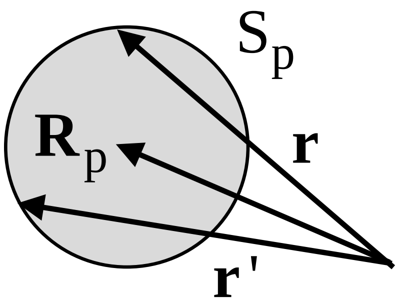
$$\mathbf{V}_p + \mathbf{\Omega}_p \times \left(\mathbf{r} - \mathbf{R}_p\right) - \mathbf{u}_\infty(\mathbf{r}) = \int_{S_p} dS' \, \mathbf{T}_0(\mathbf{r} - \mathbf{r}') \cdot \mathbf{f}^{(s)}(\mathbf{r}') \qquad (\mathbf{r} \in S_p)$$

$$-\nabla p_\infty(\mathbf{r}) + \eta_0 \Delta \mathbf{u}_\infty(\mathbf{r}) = 0 \qquad \nabla \cdot \mathbf{u}_\infty(\mathbf{r}) = 0 \qquad \text{(homog. Stokes eq.)}$$

$$\Rightarrow \Delta p_\infty(\mathbf{r}) = 0 \quad \Rightarrow \boxed{\Delta \Delta \mathbf{u}_\infty(\mathbf{r}) = 0}$$

(**bi - harmonic** $\longrightarrow$ mean - value property:

$$\left\langle \mathbf{u}_\infty(\mathbf{r}) \right\rangle_{S_P} \equiv \frac{1}{4\pi a^2} \int_{S_p} dS \, \mathbf{u}_\infty(\mathbf{r}) = \mathbf{u}_\infty(\mathbf{R}_p) + \frac{a^2}{6} \left(\nabla^2 \mathbf{u}_\infty\right)(\mathbf{R}_p)$$



- Integrate over S_p w/r to **r**, use mean-value theorem and

$$\frac{1}{4\pi a^2} \int_{S_i} dS \, \mathbf{T}_0(\mathbf{r} - \mathbf{r}') = \frac{1}{6\pi \eta_0 a} \mathbf{1} \qquad |\mathbf{r}' - \mathbf{R}_p| \le a$$

- Translational Faxén law for single sphere in ambient flow

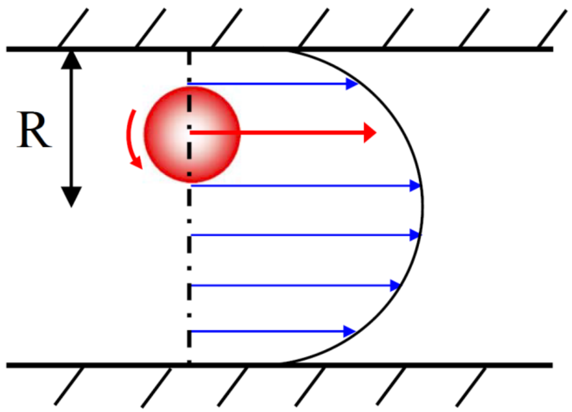
$$\mathbf{F}_p^h = -6\pi\eta_0 a\left[\mathbf{V}_p - \left(\mathbf{1} + \frac{a^2}{6}\nabla^2\right)\mathbf{u}_\infty(\mathbf{r} = \mathbf{R}_p)\right]$$

- translational Faxén law
- Stokes friction law when $\mathbf{u}_\infty = 0$

extra flow contribution

- Rotational Faxén law:

$$\mathbf{T}_p^h = -8\pi\eta_0 a^3\left[\mathbf{\Omega}_p - \frac{1}{2}\nabla\times\mathbf{u}_\infty(\mathbf{R}_p)\right]$$



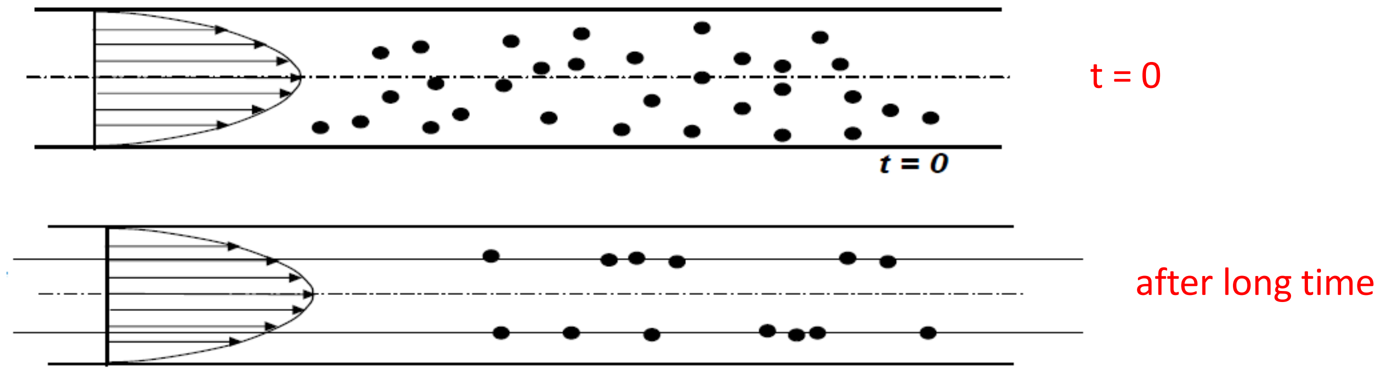
$$\mathbf{F}^h = \mathbf{0} = \mathbf{T}^h \ :$$

$$\mathbf{V}_i = \left(\mathbf{1} + \frac{a^2}{6}\nabla^2\right)\mathbf{u}_\infty(\mathbf{R}_i)$$

$$\mathbf{\Omega}_i = \frac{1}{2}\nabla\times\mathbf{u}_\infty(\mathbf{R}_i)$$

- Freely mobile particle advects with (surface-averaged) ambient flow at its center
- No cross – streamline migration for Re → 0

- Tubular pinch or Segré-Silberberg effect in pipe flow for Re > 0



Lift force drives particles towards ring at r / R ≈ 0.6 (inertia effect)

F. Feuillebois, *Perturbation problems at low Reynolds numbers,* Institute of Fundamental Technological Research Lectures, Warsaw (2004)

- Shear-induced migration from high-shear to low-shear region (pipe center) for non-Brownian spheres even at Re → 0, provided:
  - high concentration (many-particle HI effect)
  - sufficiently strong shear

2.5 Many-spheres HIs: Rotne-Prager approximation

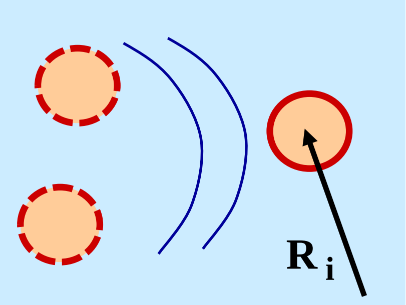
- Identify ambient flow with incident flow on sphere i by N - 1 spheres (quiescent fluid)

$$-\mu_0^t \mathbf{F}_i^h = \mathbf{V}_i - \left(\mathbf{1} + \frac{a^2}{6}\Delta_i\right) \sum_{k \neq i}^{N} \int_{S_j} dS' \, \mathbf{T}_0(\mathbf{r}' - \mathbf{R}_i) \cdot \mathbf{f}_k^{(s)}(\mathbf{r}')$$

Faxén law

- Consider dilute suspension where : $|\mathbf{R}_i - \mathbf{R}_k| \gg a$

$$\mathbf{f}_k^{(s)}(\mathbf{r}') \approx -\mathbf{F}_k^h / \left(4\pi a^2\right)$$



- Use mean-value theorem for integral over the S_k

- **Rotne – Prager approximation for t - t mobilities :**

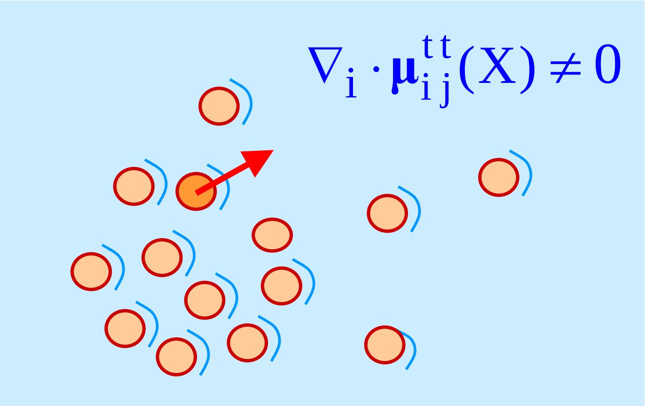
$$\mathbf{V}_i \approx -\sum_{j=1}^{N} \mu_0 \left\{\mathbf{1}\delta_{ij} + (1-\delta_{ij})\mathbf{T}_{RP}(\mathbf{R}_i - \mathbf{R}_j)\right\} \cdot \mathbf{F}_j^h = -\sum_{j=1}^{N} \boldsymbol{\mu}_{ij}^{RP}\left(\mathbf{R}_{ij}\right) \cdot \mathbf{F}_j^h$$

$$\mathbf{T}_{RP}(\mathbf{r}) = \frac{3}{4}\left(\frac{a}{r}\right)\left(\mathbf{1} + \hat{\mathbf{r}}\hat{\mathbf{r}}\right) + \frac{1}{2}\left(\frac{a}{r}\right)^3\left(\mathbf{1} - 3\hat{\mathbf{r}}\hat{\mathbf{r}}\right) \quad (\rightarrow 0 \text{ for } r \rightarrow \infty)$$

Rotne – Prager approximation

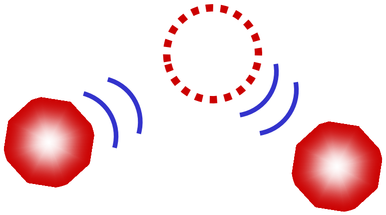
$$\begin{pmatrix} V \\ \Omega \end{pmatrix} = -\begin{pmatrix} \mu^{tt}(X) & \mu^{tr}(X) \\ \mu^{rt}(X) & \mu^{rr}(X) \end{pmatrix} \cdot \begin{pmatrix} F^h \\ T^h = 0 \end{pmatrix}$$

$$\nabla_i \cdot \mu_{ij}^{RP}(\mathbf{R}_{ij}) = 0$$



hydrodynamic drift part:
from low to high mobility region

- Pros and cons:



⊕ Positive definiteness of 3N x 3N matrix $\mu^{tt}(X)$ is preserved

⊕ Easy to apply (theory & simulation)

⊕ Upper bound to exact $\mu^{tt}(X)$

⊖ All flow reflections neglected, lubrication neglected

⊖ Overestimates HI in general

➡ Multipole expansions including reflections / many - body HI & lubrication

General method: **Hydrodyn. multipoles method by Cichocki and collaborators**

Hyrodynamic cluster expansion

$$\boldsymbol{\mu}^{tt}_{ij}(X) = \mu_0 \mathbf{1}\delta_{ij} + \underbrace{\Delta\mu^{(2)}_{ij}(X)}_{\text{2 - body HI}} + \underbrace{\Delta\mu^{(3)}_{ij}(X)}_{\text{3 - body HI}} + \ldots$$

$$\begin{cases} O(r^{-4}): \; i \neq j \\ O(r^{-7}): \; i = j \end{cases}$$

$$\Delta\boldsymbol{\mu}^{(2)}_{ij}(X) = \mu_0 \left[\delta_{ij} \sum_{p \neq i}^{N} \boldsymbol{\omega}_{11}(\mathbf{R}_{ip}) + (1-\delta_{ij})\boldsymbol{\omega}_{12}(\mathbf{R}_{ij}) \right]$$

pairwise - additive

- Long - distance multipole expansion of 2 - body HI :

$$\boldsymbol{\omega}_{12}(\mathbf{r}) = \underbrace{\underbrace{\frac{3}{4}\left(\frac{a}{r}\right)\left[1+\hat{\mathbf{r}}\hat{\mathbf{r}}\right]}_{\text{Oseen term}} + \underbrace{\frac{1}{2}\left(\frac{a}{r}\right)^3\left[1-3\hat{\mathbf{r}}\hat{\mathbf{r}}\right]}_{\text{dipole term}}}_{\text{Rotne - Prager part}} + \underbrace{O\left(r^{-7}\right)}_{\text{back reflections}}$$

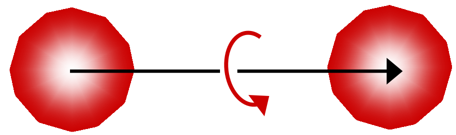
$$\boldsymbol{\omega}_{11}(\mathbf{r}) = \underbrace{-\frac{15}{4}\left(\frac{a}{r}\right)^4}_{\text{first self reflection}} \hat{\mathbf{r}}\hat{\mathbf{r}} + O\left(r^{-6}\right)$$

- Rotne - Prager (RP) part suffices for semi-dilute charge - stabilized dispersions !

Two - spheres translational mobilities in infinite fluid

- axial symmetry and isotropy

$$\begin{pmatrix} \mathbf{V}_1 \\ \mathbf{V}_2 \end{pmatrix} = \mu_0 \begin{pmatrix} \mathbf{1} + \boldsymbol{\omega}_{11} & \boldsymbol{\omega}_{12} \\ \boldsymbol{\omega}_{21} & \mathbf{1} + \boldsymbol{\omega}_{22} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{F}_1 \\ \mathbf{F}_2 \end{pmatrix}$$

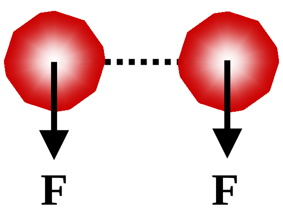


$$\mathbf{r} = \mathbf{R}_2 - \mathbf{R}_1$$

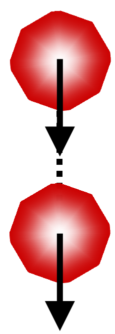
$$\boldsymbol{\omega}_{12} = \boldsymbol{\omega}_{21} \qquad \boldsymbol{\omega}_{11} = \boldsymbol{\omega}_{22}$$

$$\boldsymbol{\omega}_{ij}(\mathbf{r}) + \delta_{ij}\mathbf{1} = x_{ij}(r)\,\hat{\mathbf{r}}\hat{\mathbf{r}} + y_{ij}(r)\left[\mathbf{1} - \hat{\mathbf{r}}\hat{\mathbf{r}}\right]$$

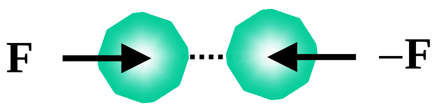
- known recursion relations for (a / r) expansion & lubrication corrections



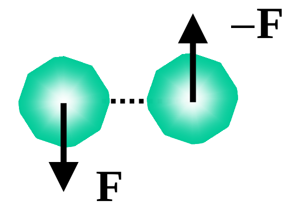
$$\mathbf{V}_i = \mathbf{V}_{sed} = (y_{11} + y_{12})\mu_0 \mathbf{F}$$



$$\mathbf{V}_{sed} = (x_{11} + x_{12})\mu_0 \mathbf{F}$$



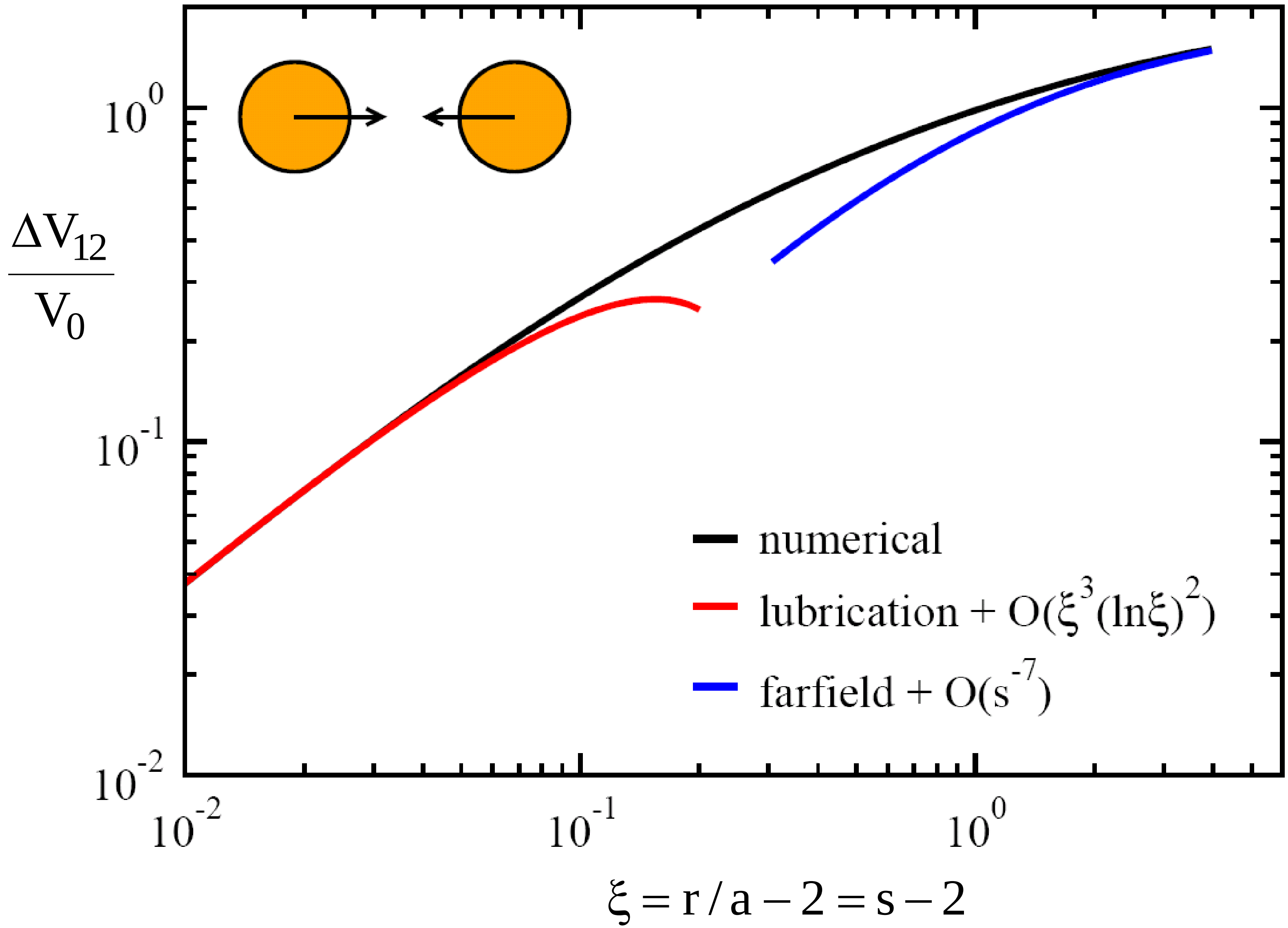
$$\Delta\mathbf{V}_{12} = 2(x_{11} - x_{12})\mu_0 \mathbf{F}$$



$$\Delta\mathbf{V}_{12} = 2(y_{11} - y_{12})\mu_0 \mathbf{F}$$

Jeffrey & Onishi, J. Fluid Mech. **139** (1984)

Jones & Schmitz, Physica A **149** (1988)



- Lubrication important for relative pair motion close to contact
- **Not probed for electrically repelling colloids**

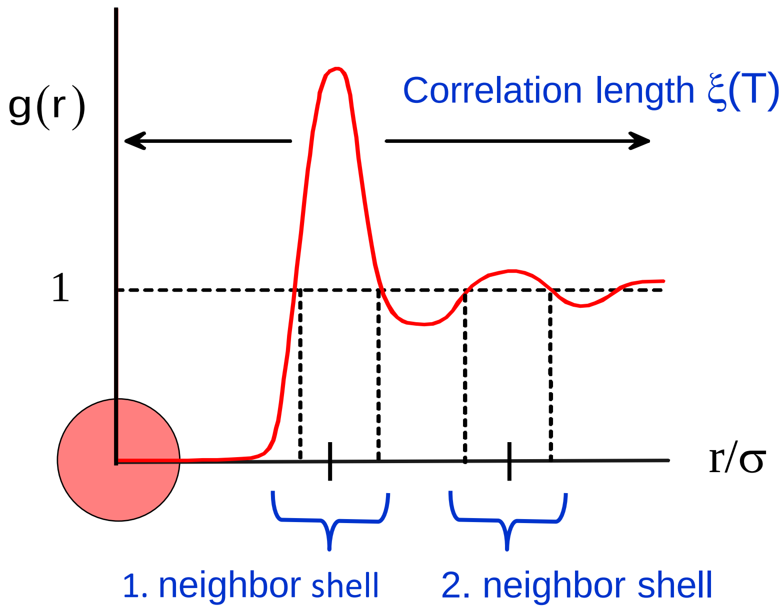
Content

3. Salient static properties

- Pair distribution function
- Methods of calculation
- Ionic mixtures
- Effective colloid interactions
- Poisson-Boltzmann theory of microions
- Force on colloidal particle in electrolyte

3.1 Pair distribution function

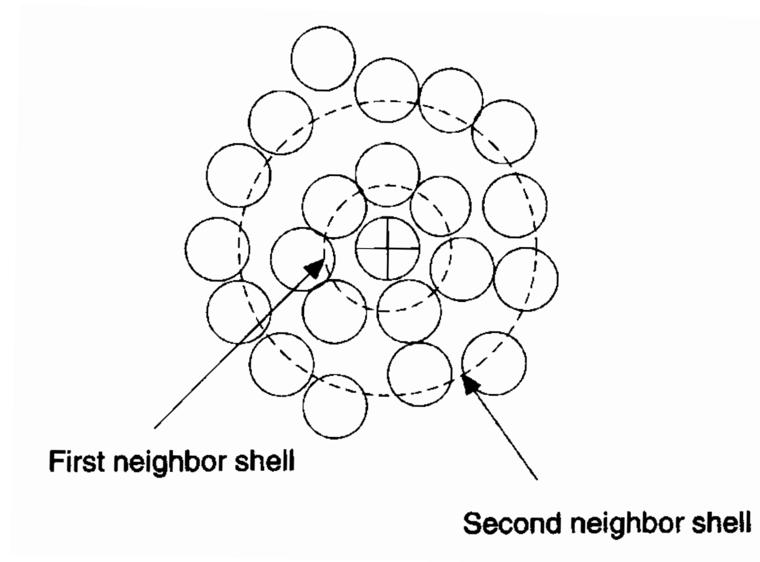
- g(r) = cond. probability of finding another particle at distance r



$$g(r) = \lim_{\infty} \frac{\langle N(r, r+\Delta r)\rangle_{eq}}{\rho\, 4\pi r^2 \Delta r} \rightarrow 1$$

ideal gas

fluid near-field order

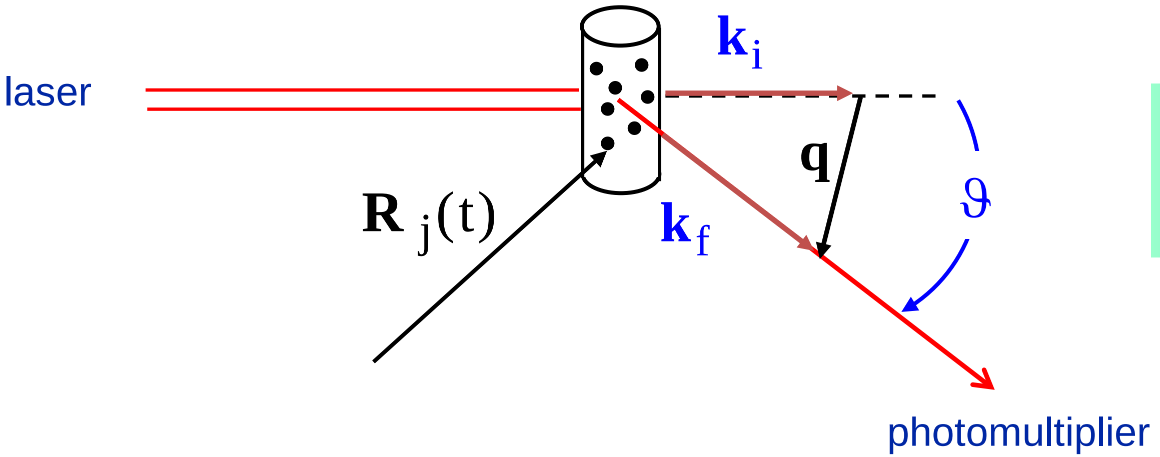


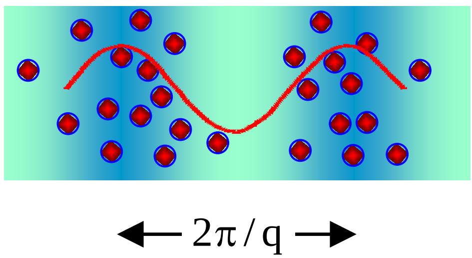
$$g(|\mathbf{r}-\mathbf{r}'|) = \lim_{\infty} V^2 \langle \delta(\mathbf{r}-\mathbf{R}_1)\,\delta(\mathbf{r}'-\mathbf{R}_2)\rangle_{eq}$$

homogeneous

isotropic

Relation to colloid scattering experiments: Static structure factor S(q)



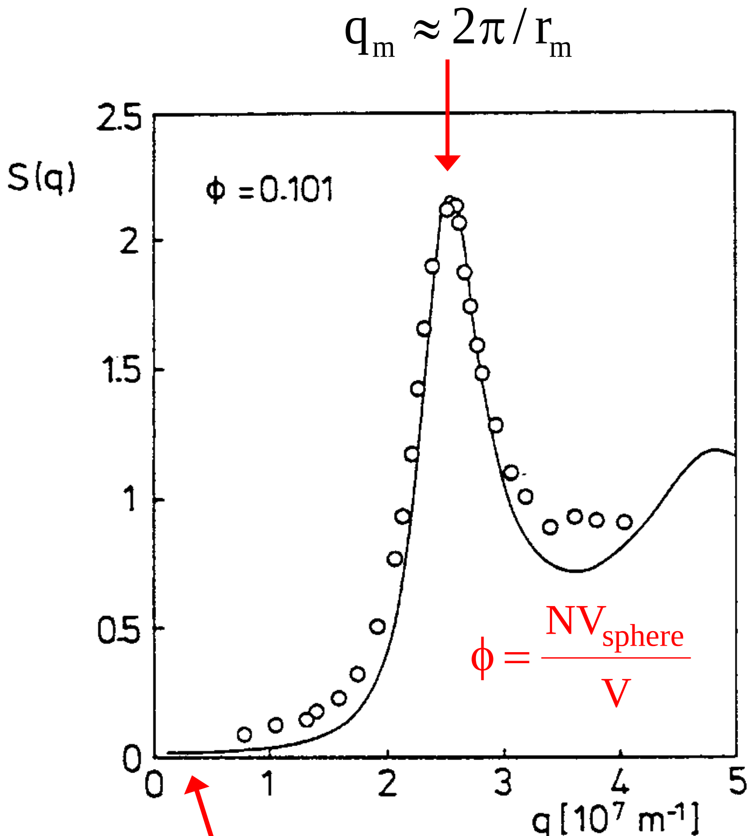


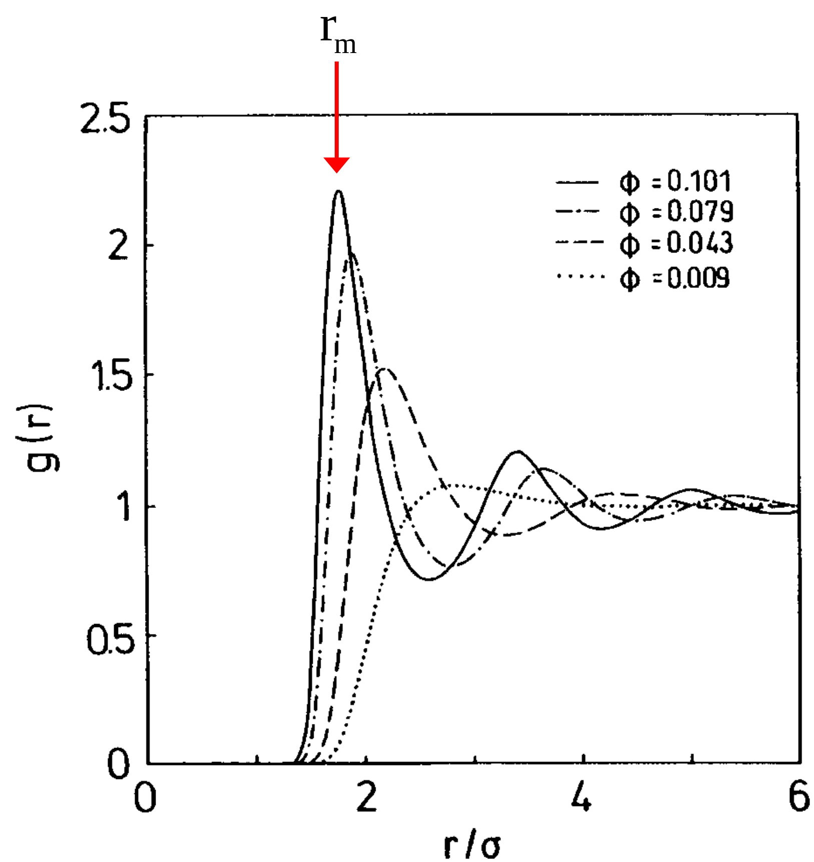
$$I(q) \propto \langle N \rangle P(q) S(q)$$: for single and quasi-elastic scattering $$q = \frac{4\pi}{\lambda}\sin\left[\frac{\vartheta}{2}\right]$$

$$S(q) = \lim_{\infty} \left\langle \frac{1}{N} \sum_{\mathbf{l},\mathbf{j}=1}^{N} \exp\left\{ i\, \mathbf{q} \cdot \left[\mathbf{R}_l(0) - \mathbf{R}_j(0) \right] \right\} \right\rangle_{eq} = 1 + n \int d\mathbf{r} \exp\{ i\, \mathbf{q} \cdot \mathbf{r} \} [g(r) - 1]$$

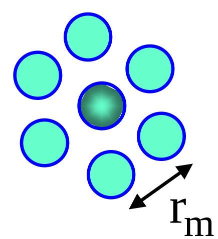
$$g(r) = 1 + \mathrm{FT}^{-1}\left[\frac{S(q) - 1}{n} \right]$$

g(r) and S(q) for dispersion of Yukawa colloidal spheres





$$\lim_{q\to 0} S(q) = k_B T \left(\frac{\partial n}{\partial \Pi_{coll}}\right)_{T,\mu_s,\{\mu_\alpha \neq \mu_{coll}\}}$$



particle cage

3.2 Methods of calculation

- Introduce total correlation function : $h(r_{12}) := g(r_{12}) - 1$

- Define direct correlation function c(r) through Ornstein-Zernike equation :

$$h(r_{12}) = c(r_{12}) + n\int d\mathbf{r}_3\, c(r_{13})\, h(r_{23})$$

total correlations of 1 and 2 — direct correlations — indirect correlations of 1 and 2 through particles 3,4,...

$$h(r_{12}) = c(r_{12}) + n\int d\mathbf{r}_3\, c(r_{13})\, c(r_{23}) + n^2 \int d\mathbf{r}_3 d\mathbf{r}_4\, c(r_{13})\, c(r_{24})\, c(r_{34}) + 0(c^4)$$

- General properties of c(r) : $c(r) = -\beta\, u(r), \quad r \to \infty$ valid for all densities

Important closure relations c(r) = F[u(r),h(r)]

- Rescaled mean spherical approximation (RMSA) :

$$c(r) = -\beta u(r), \quad r > \sigma_{eff} > \sigma \qquad g(r = \sigma_{eff}^{+}) = 0$$

- Hypernetted chain approximation (HNC)

  (energy and virial routes give same pressure, g(r) > 0 is guaranteed)

$$c(r) = e^{-\beta u(r)} \cdot e^{\gamma(r)} - \gamma(r) - 1 \qquad \gamma(r) := h(r) - c(r)$$

- Percus - Yevick approximation (PY)

$$c(r) = e^{-\beta u(r)} \cdot [1 + \gamma(r)] - \gamma(r) - 1$$

- Rogers - Young mixing scheme (RY): thermodynamically partially self-consistent

$$c(r) = e^{-\beta u(r)} \cdot \left[1 + \frac{\exp\{\gamma(r) f(r)\} - 1}{f(r)}\right] - \gamma(r) - 1 \qquad f(r) = 1 - e^{-\alpha r}$$

$\alpha \to \infty$: HNC

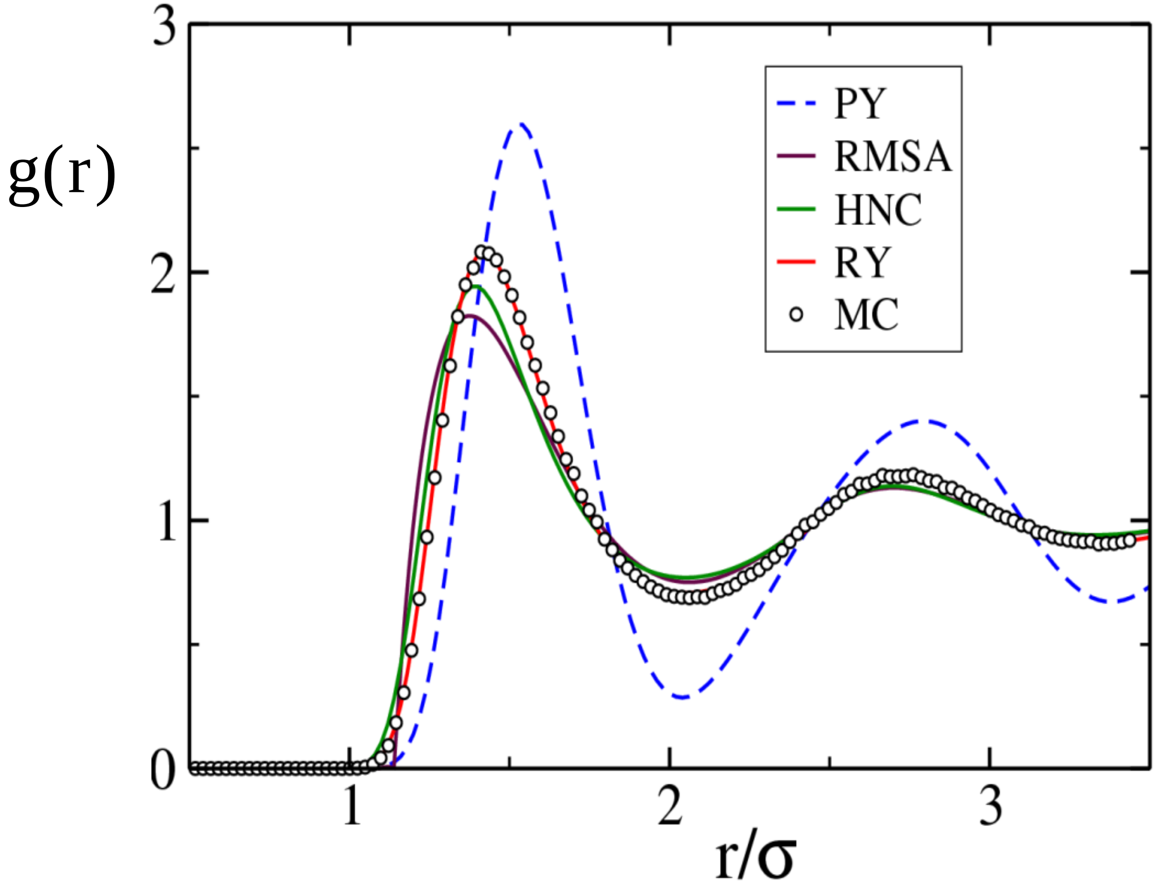
$\alpha \to 0$: PY

$$\chi_T^{Virial} = \chi_T^{Compr}$$

determines α

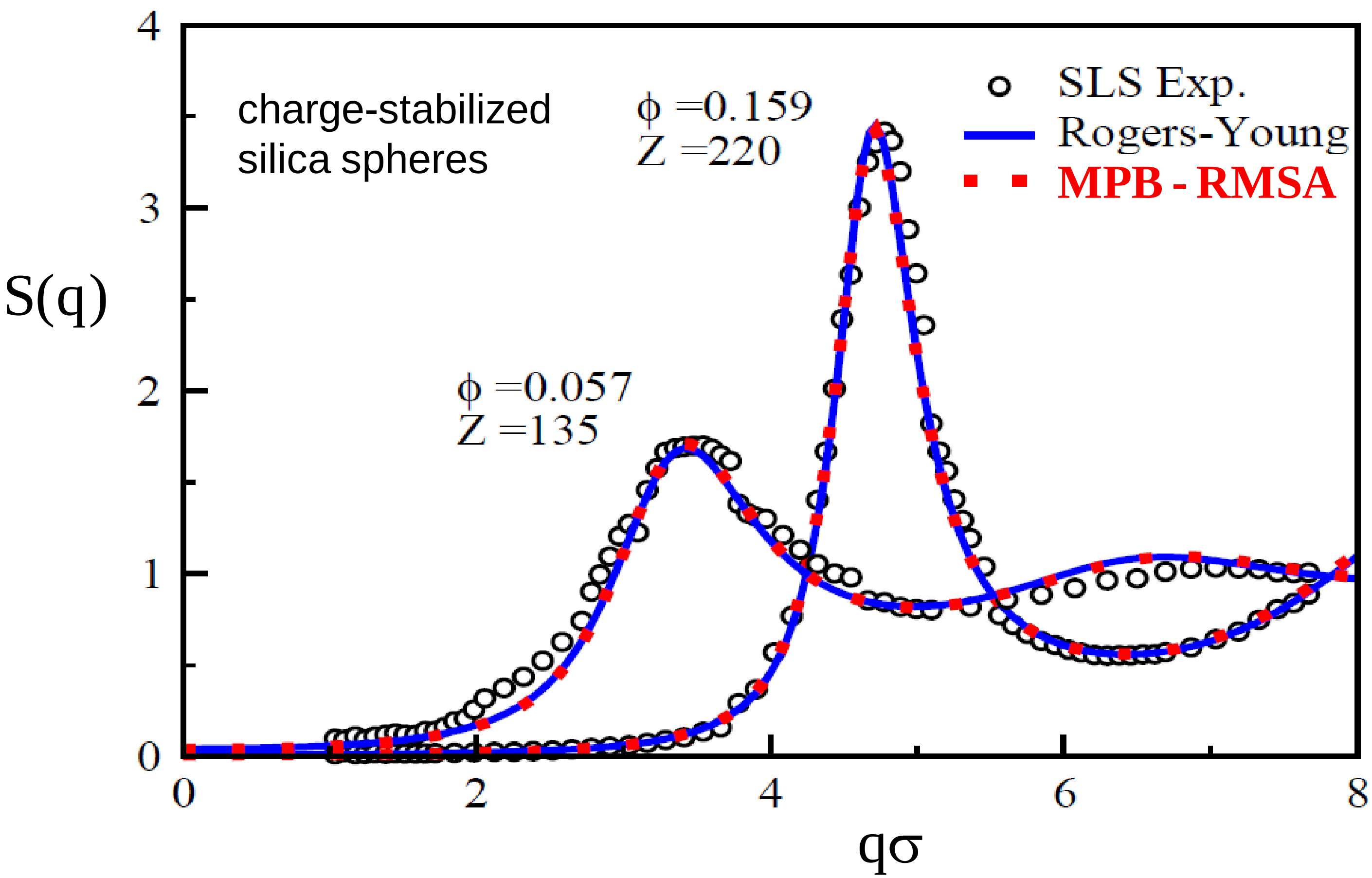
Performance check versus MC simulation

Screened Coulomb potential:



- RY hybrid scheme performs best but is numerically most costly

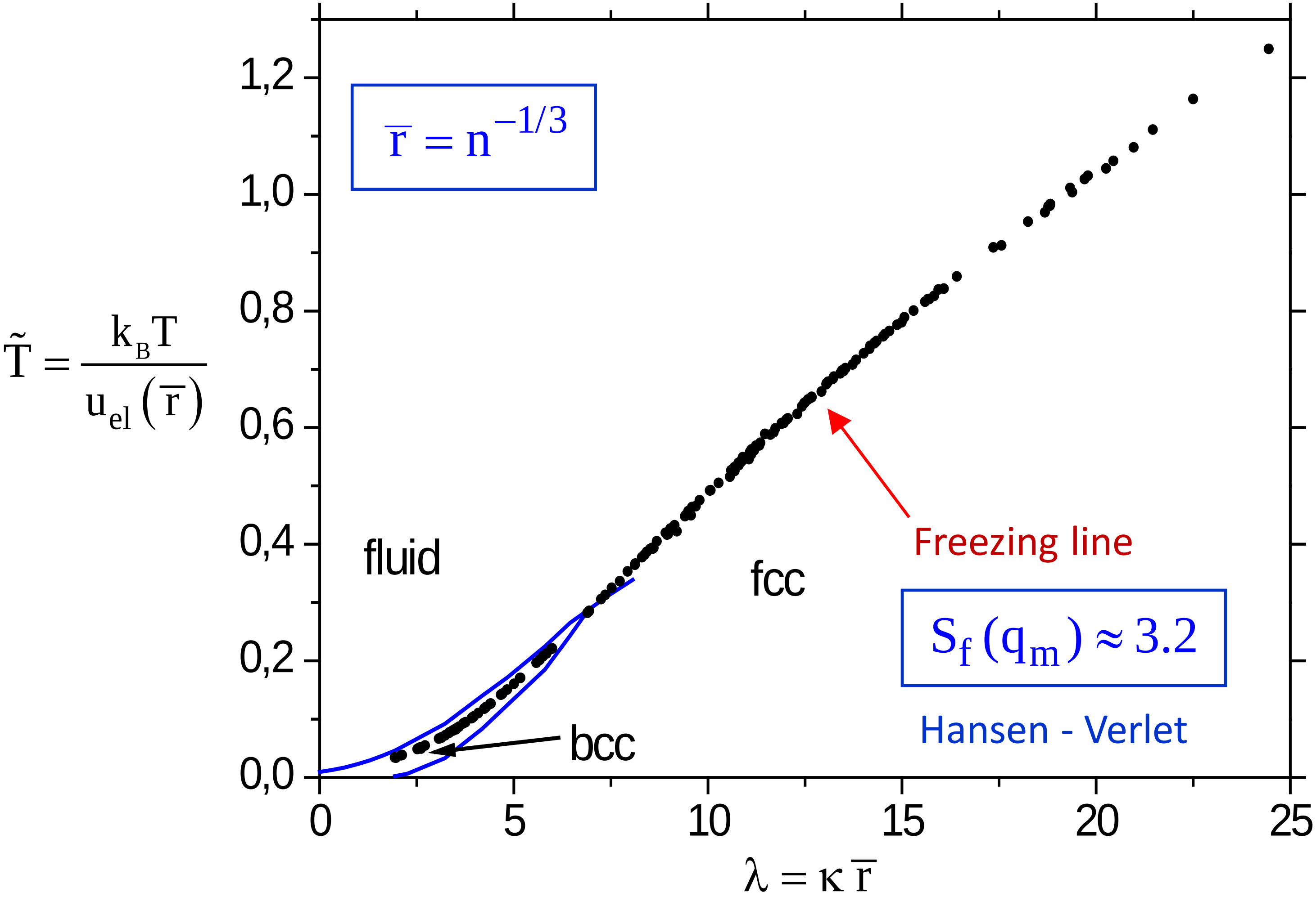
New analytic method to calculate static structure factor



MPB - RMSA: scheme close to experiment, simulation & RY scheme highly efficient

Heinen, Holmqvist, Banchio & Nägele, J. Chem. Phys. **134,** 04453**2** & 129901 (2011)

Universal phase diagram for Yukawa – type charge-stabilized spheres



- $\{Z, n, n_s, a, L_B\} \rightarrow (\tilde{T}, \lambda)$ single phase point
- Discuss dynamics in fluid regime only !

Gapinski, Patkovski, Nägele
J. Chem. Phys. **136** (2012)

3.3 Ionic mixtures

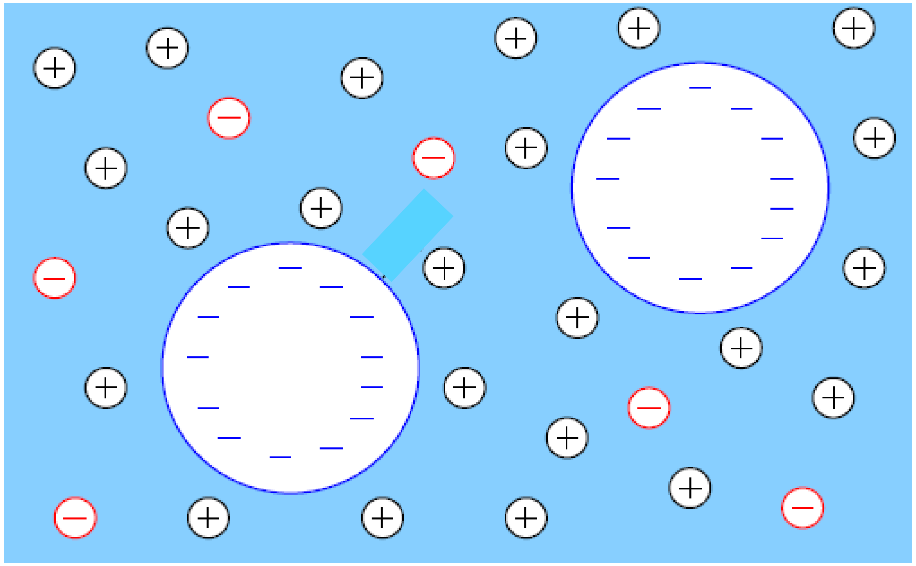
Primitive model of ionic systems

- Macroions and microions treated as uniformly charged hard spheres
- Colloidal electrokinetics & electrolyte transport

$$u_{\alpha\beta}(r) = u_{\alpha\beta}^{HS}(r) + u_{\alpha\beta}^{C}(r)$$

$$\frac{u_{\alpha\beta}^{C}(r)}{k_B T} = L_B \frac{z_\alpha z_\beta}{r} \quad , r > \left(a_\alpha + a_\beta\right)$$

$$\sum_{\alpha=1}^{m} n_\alpha z_\alpha = 0$$



- no polarization
- structureless Newtonian solvent

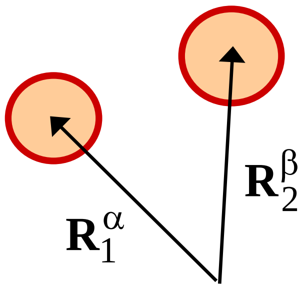
water at 20º C : $L_B = 0.71\text{nm}$

$\eta_0 = 1 \times 10^{-3}\ \text{Pa} \cdot \text{s}$

PM equilibrium pair distribution functions

- Cond. probability of finding ion of type β at distance r from ion of type α

$$g_{\alpha\beta}(|\mathbf{r}-\mathbf{r}'|) = h_{\alpha\beta}+1 = \frac{1}{n_\alpha n_\beta}\lim_{\infty} V^2 \left\langle \delta\left(\mathbf{r}-\mathbf{R}_1^\alpha\right)\delta\left(\mathbf{r}'-\mathbf{R}_2^\beta\right)\right\rangle_{eq}$$



- m-component Ornstein - Zernike equations:

$$h_{\alpha\beta}(r) = c_{\alpha\beta}(r) + \sum_{\gamma=1}^{m} n_\gamma \int d\mathbf{r}\, c_{\alpha\gamma}(|\mathbf{r}-\mathbf{r}'|)\, h_{\beta\gamma}(r')$$

$$c_{\alpha\beta}(r \gg \zeta(T)) = -u_{\alpha\beta}(r)/k_B T$$

- Fourier - transformed OZ m×m matrix equation:

$$[\mathbf{1}+\mathbf{H}(q)]\cdot[\mathbf{1}-\mathbf{C}(q)] = \mathbf{1}$$

$$C_{\alpha\beta}(q) = \left(n_\alpha n_\beta\right)^{1/2} c_{\alpha\beta}(q) \qquad H_{\alpha\beta}(q) = \left(n_\alpha n_\beta\right)^{1/2} h_{\alpha\beta}(q)$$

- Symmetric matrix **S**(q) of partial **static** structure factors: $\mathbf{S}(q) = [\mathbf{1}-\mathbf{C}(q)]^{-1}$

$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + \left(n_\alpha n_\beta\right)^{1/2} \int d\mathbf{r} \exp\{i\,\mathbf{q}\cdot\mathbf{r}\} h_{\alpha\beta}(r)$$

Exact local electroneutrallity condition

$$C_{\alpha\beta}(q) = C^{(s)}_{\alpha\beta}(q) - 4\pi L_B \frac{(n_\alpha n_\beta)^{1/2} z_\alpha z_\beta}{q^2}$$

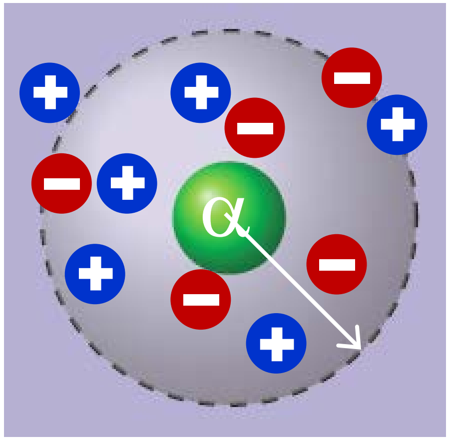
$$FT^{3D}\left[\frac{1}{r}\right] = \frac{4\pi}{q^2}$$

short-range correlations, regular function at q = 0

- From regular expansion of H(q) and $C^{(s)}$(q) at q = 0:

$$N^{(\alpha)}_{el}(R) = \sum_{\gamma=1}^{m} n_\gamma z_\gamma 4\pi \int_0^R dr\, r^2 \left[h_{\alpha\gamma}(r) + 1\right]$$

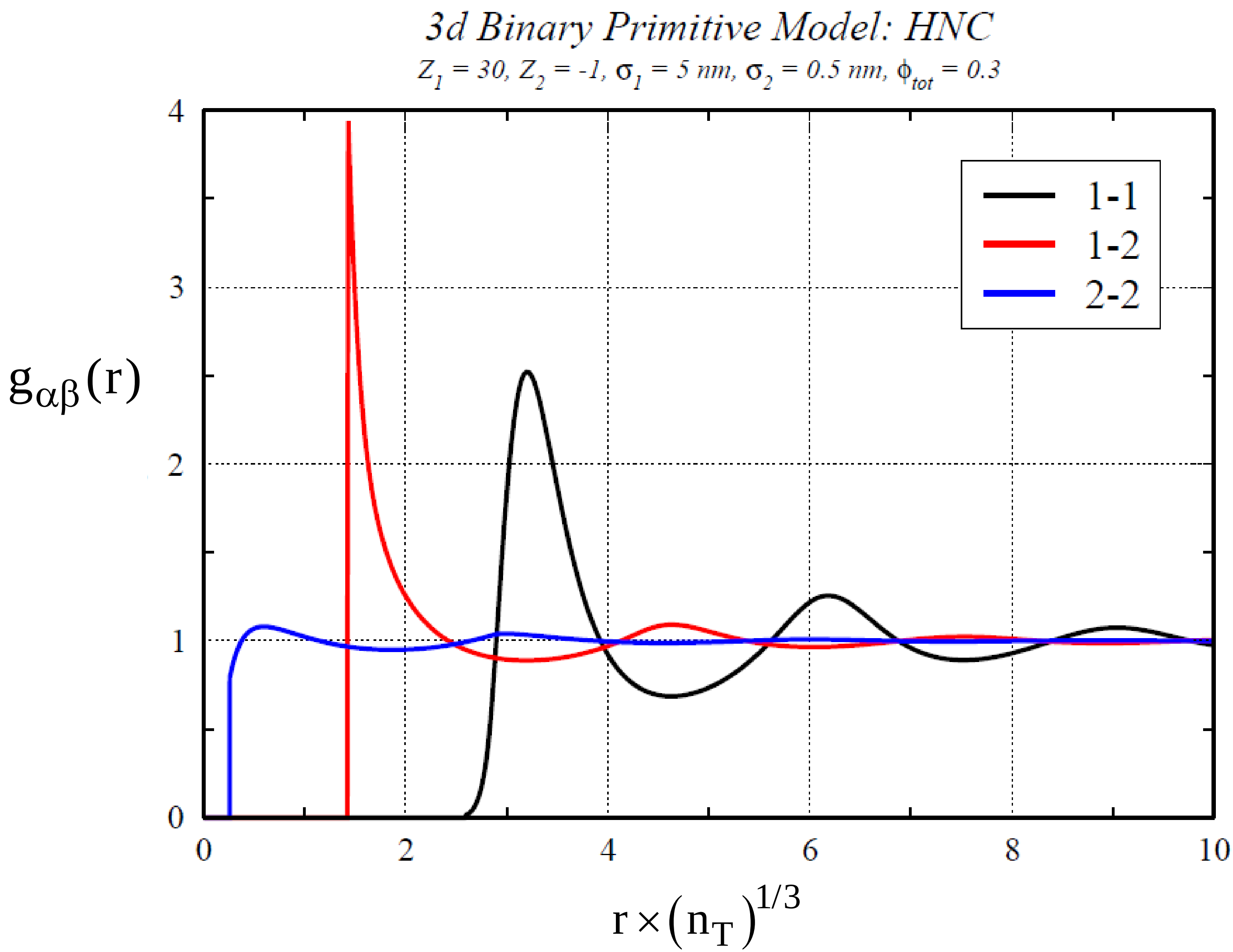
$$N^{(\alpha)}_{el}(R \to \infty) = -z_\alpha \quad (\alpha = 1, \ldots, m)$$



mean charge number in sphere of radius R

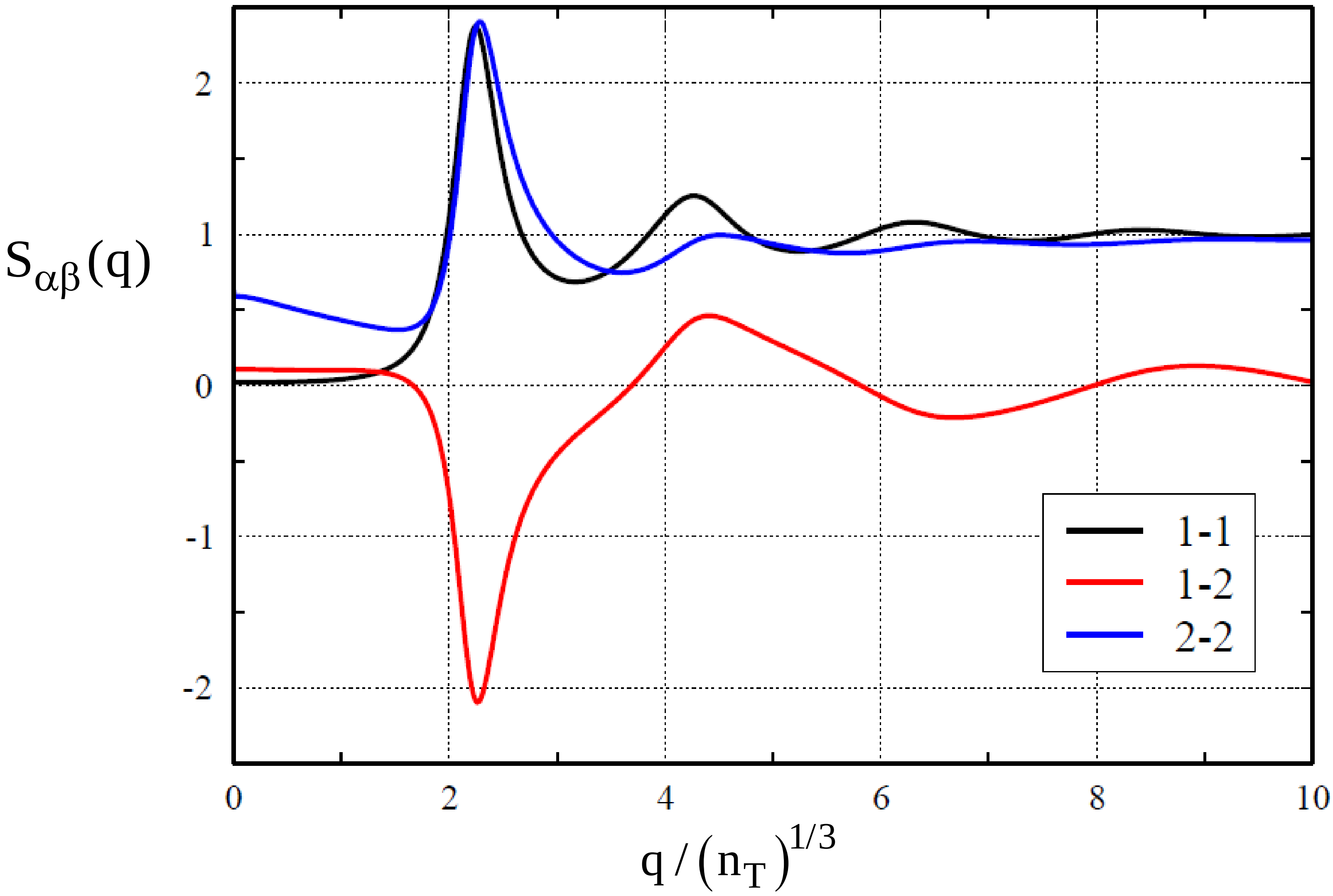
- It follows for binary ionic mixture:

$$|z_1| S_{11}(0) = |z_2| S_{22}(0) = (|z_1 z_1|)^{1/2} S_{12}(0)$$

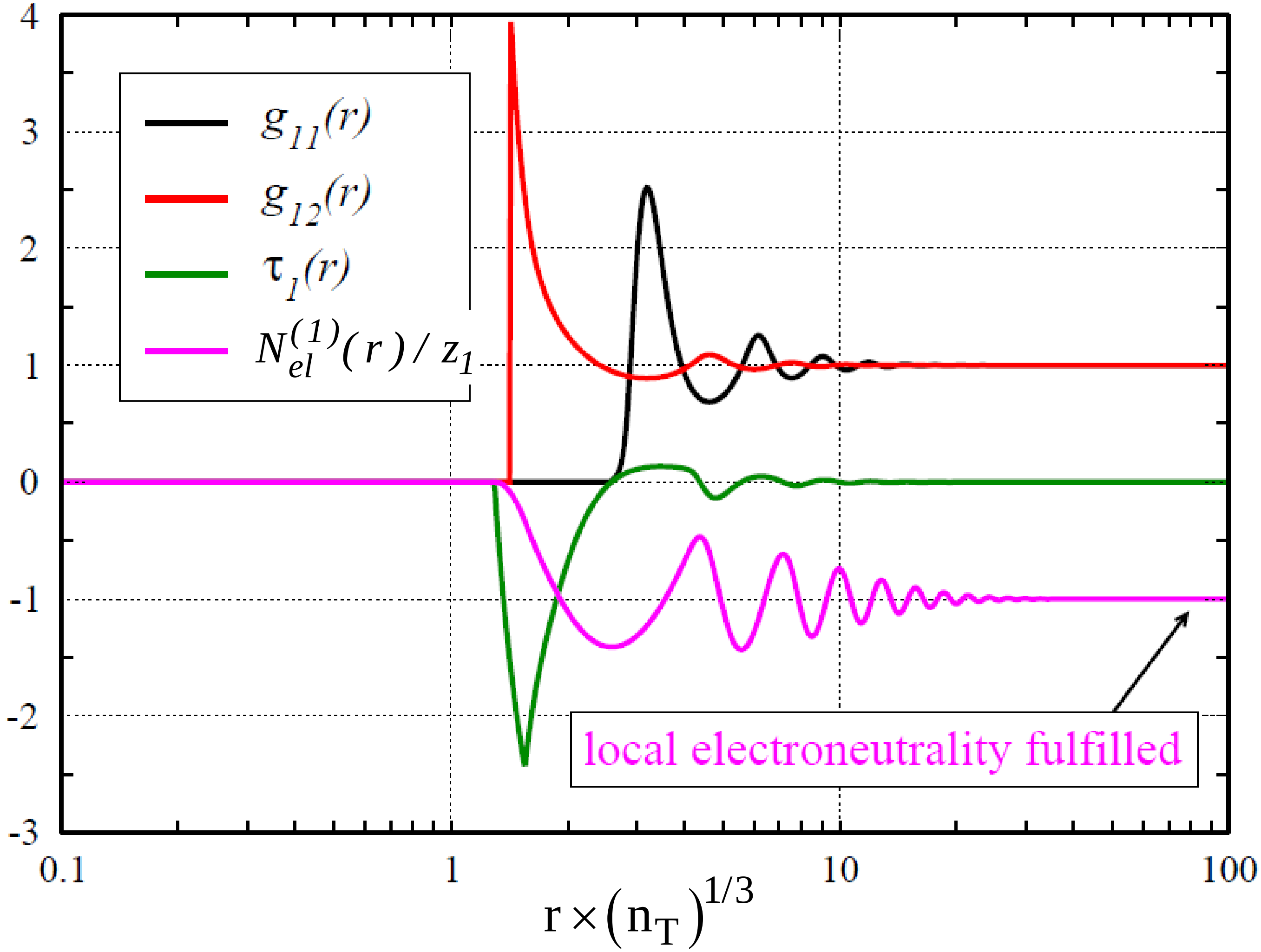


HNC calculations, courtesy by: Marco Heinen, Düsseldorf University

$$|z_1| S_{11}(0) = |z_2| S_{22}(0) = \left(|z_1 z_1|\right)^{1/2} S_{12}(0)$$



$$N_{el}^{(\alpha)}(r \to \infty) = -z_\alpha \quad (\alpha = 1, \ldots, m)$$



- Charge-charge global structure factor for m - component PM

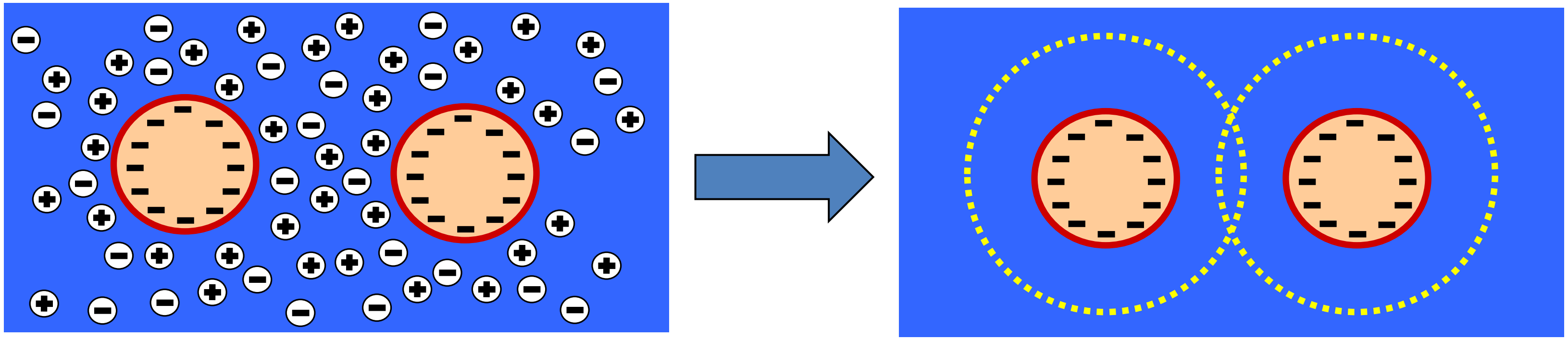
$$\delta\rho_{el}(\mathbf{r}) = \sum_{\alpha=1}^{m} z_\alpha \sum_{j=1}^{N_\alpha} \delta\left(\mathbf{r} - \mathbf{R}_j^\alpha\right) - \langle \rho_{el} \rangle_{eq}$$

$$S_{ZZ}(q) = \frac{1}{n_T \left\langle z^2 \right\rangle} \int d^3(\mathbf{r}-\mathbf{r}') \exp\left\{ i\, \mathbf{q} \cdot (\mathbf{r}-\mathbf{r}') \right\} \left\langle \delta\rho_{el}(\mathbf{r}) \delta\rho_{el}(\mathbf{r}') \right\rangle_{eq}$$

$$S_{ZZ}(q) = \frac{1}{\left\langle z^2 \right\rangle} \sum_{\alpha,\beta=1}^{m} \left(x_\alpha x_\beta \right)^{1/2} z_\alpha z_\beta S_{\alpha\beta}(q) \rightarrow \frac{q^2}{\kappa^2} + O\left(q^4\right)$$

Long - wavelength charge density fluctuations are offset since bulit-up of macroscopic electric field by thermal fluctuations is energetically too costly

3.4 Effective colloid pair potential



$$\beta u_{\alpha\beta}(r) = L_B \frac{Z_\alpha Z_\beta}{r}$$

$$\beta u_{\text{eff}}(r) = L_B Z^2 \left(\frac{\exp[\kappa a]}{1+\kappa a} \right)^2 \frac{\exp[-\kappa r]}{r}$$

- Eff. macroion - macroion potential from averaging over microionic degrees of freedom

Effective macroion potential

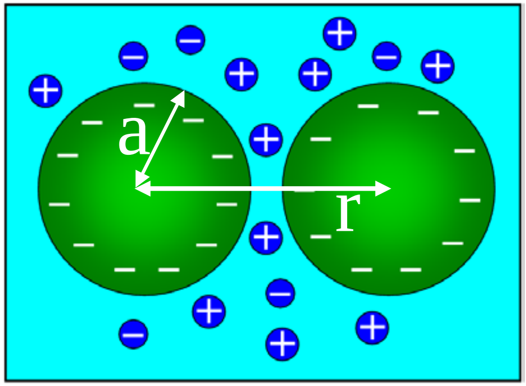
$$h_{\alpha\beta}(r) = c_{\alpha\beta}(r) + \sum_{\gamma=1}^{m} n_\gamma \int d\mathbf{r}\, c_{\alpha\gamma}(|\mathbf{r}-\mathbf{r}'|)\, h_{\beta\gamma}(r')$$

$$h_{cc}(r) = c_{eff}(r) + n_c \int d\mathbf{r}'\, c_{eff}(|\mathbf{r}-\mathbf{r}'|)\, h_{cc}(r')$$

effective macroion direct corr. function

$$c_{eff}(r \gg a_\alpha + a_\beta) = -\frac{u_{eff}(r)}{k_B T}$$

$$h_{cc}(r; n_c) \Leftrightarrow u_{eff}(r; n_c)$$ exact correspondence



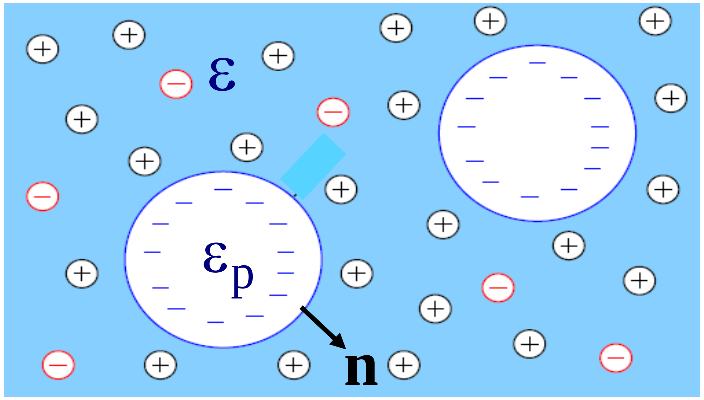
$$\{g_{cc}, g_{c+}, g_{c-}, g_{++}, g_{--}, g_{+-}\}$$

$$g_{\alpha\beta}(r) = h_{\alpha\beta}(r) + 1$$

$$c^{MSA}_{\alpha\beta}(r) = -\frac{u_{\alpha\beta}(r)}{k_B T}, \quad r > (a_\alpha + a_\beta)$$ MSA closure for all ionic components

$$\Rightarrow \quad \frac{u_{eff}(r)}{k_B T} = L_B Z^2 \left(\frac{\exp[\kappa a]}{1+\kappa a}\right)^2 \frac{\exp[-\kappa r]}{r} \quad (r > 2a) \qquad (n_c \to 0)$$

3.5 Poisson-Boltzmann theory of microions



- **Colloids:** N spatially fixed dielectric spheres in infinite m-component electrolyte act as static external potential for small **mobile micoions** (m components)
- Born – Oppenheimer picture of microions
- Apply equil. density functional theory (DFT) to grand free energy functional:

$$\Omega\left[\{\rho_\alpha\};X\right] = A^{id}\left[\{\rho_\alpha\}\right] + A^{MF}\left[\{\rho_\alpha\}\right] + A^{corr}\left[\{\rho_\alpha\}\right] - \sum_{\alpha=1}^{m} \int d^3r\,\rho_\alpha(\mathbf{r})\left[\mu_\alpha^\infty - V_\alpha^{ex}(\mathbf{r};X)\right]$$

$$A^{id} = k_B T \sum_{\alpha=1}^{m} \int d^3r\,\rho_\alpha(\mathbf{r})\left[\ln\left(\Lambda_\alpha^3\,\rho_\alpha(\mathbf{r})\right) - 1\right]$$

$$A^{MF} = \frac{1}{2}\int d^3r \int d^3r'\,\frac{\rho_{el}(\mathbf{r})\rho_{el}(\mathbf{r}')}{\varepsilon\left|\mathbf{r}-\mathbf{r}'\right|}$$

$$V_\alpha^{ex}(\mathbf{r};X) = z_\alpha e \psi^{ex}(\mathbf{r};X) + V_{sr}^{ex}(\mathbf{r};X)$$

colloid's excluded volumes

- Microion charge density trial function:

$$\rho_{el}(\mathbf{r}) = \sum_{\alpha=1}^{m} z_\alpha e\,\rho_\alpha(\mathbf{r})$$

- electric potential due to fixed macroions:

$$\psi^{ex}(\mathbf{r},X) = \int d^3r'\,\frac{\rho_{el}^{ex}(\mathbf{r}';X)}{\varepsilon_p\left|\mathbf{r}-\mathbf{r}'\right|}$$

- Mermin variational principle (1965): equilibrium microion profiles minimize Ω

$$\Omega\left[\{n_\alpha + \delta n_\alpha\}\right] - \Omega\left[\{n_\alpha\}\right] = 0 + \left\|(\delta n_\alpha)^2\right\|$$

$$\Omega\left[\{n_\alpha\};X\right] = \Omega_{eq}\left[\{n_\alpha\};X\right]$$

- Neglect short-range microion electro-steric correlations: $A^{corr} = 0$

$\longrightarrow$ Euler-Lagrange eqns. for „electro - chemical“ microion potentials:

$$\mu_\alpha^\infty = k_B T \ln\left[\Lambda_\alpha^3 n_\alpha(\mathbf{r};X)\right] + z_\alpha e\psi(\mathbf{r};X) + V_{sr}^{ex}(\mathbf{r};X)$$

field-free
electrolyte reservoir

$$\psi(\mathbf{r};X) = \int d^3r' \, \frac{n_{el}(\mathbf{r}';X)}{\varepsilon|\mathbf{r}-\mathbf{r}'|} + \psi^{ex}(\mathbf{r};X)$$

• **total** equil. mean electric potential

$$n_\alpha(\mathbf{r};X) = n_\alpha^\infty \exp\{-z_\alpha e\psi(\mathbf{r};X)/(k_B T)\} \quad (\mathbf{r} \in V_{fl})$$

$$n_\alpha^\infty = n_\alpha(\mathbf{r}\to\infty) = \exp\left\{\mu_\alpha^\infty / k_B T\right\} / \Lambda_\alpha^3$$

- Microions treated as inhomog. ideal gas of point ions (w/r to entropy) except for Coulomb forces. Each microion exists indep. in mean field of others

- Using $\Delta_{\mathbf{r}}\left(1/|\mathbf{r}-\mathbf{r}'|\right)=-4\pi\delta(\mathbf{r}-\mathbf{r}')$ → MF Poisson-Boltzmann equation for ψ

$$\Delta\psi(\mathbf{r};X)=-\frac{4\pi}{\varepsilon}\sum_{\alpha=1}^{m} n_\alpha^\infty z_\alpha e\exp\{-z_\alpha e\psi(\mathbf{r};X)/(k_BT)\}\quad(\mathbf{r}\in V_{fl}(X))\qquad \psi(\mathbf{r}\to\infty)=0$$

- Electric BCs for constant surface charge densities on N spheres:

$$(\varepsilon\nabla\psi-\varepsilon_p\nabla\psi)\cdot\mathbf{n}=-4\pi\sigma_i\quad(\mathbf{r}\in S_i,\ \varepsilon_p\ll\varepsilon\text{ for water})$$

- Standard case: q-q electrolyte:

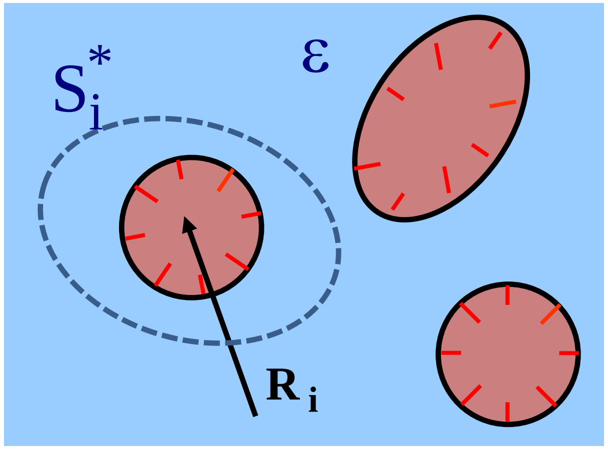
$$\Delta\phi(\mathbf{r};X)=\kappa^2\sinh[\phi(\mathbf{r};X)]\qquad \phi(\mathbf{r})=qe\psi(\mathbf{r})/(k_BT)\qquad \kappa^2=8\pi L_B c_s q^2$$

$$\Omega_{eq}^{PB}(\{n_\pm\};X)-\Omega_{eq}^{PB,res}=\frac{1}{2qe}\sum_{i=1}^{N}\sigma_i\int_{S_i}dS\,\phi(\mathbf{r})+k_BTc_s\int_{V_{fl}}d^3r\left[\phi\sinh(\phi)-2\cosh(\phi)-2\right]$$

$$\Omega_{eq}^{PB,res}=-2k_BTc\times V_{fl}=-p_{res}V_{fl}$$

linear Debye - Hückel expression

3.6 Force on colloidal particle in electrolyte



- N-1 colloids fixed and microions equilibrated
- Small displacement of colloid i:

$$d\Omega_{eq}(X) = -S\,dT - p\,dV_{fl} + \sum_{\alpha} \langle N_\alpha \rangle d\mu_\alpha - \mathbf{F}_i \cdot d\mathbf{R}_i$$

$$\mathbf{F}_i(X) = -\left(\frac{\partial \Omega_{eq}(X)}{\partial \mathbf{R}_i}\right)_{T,\{\mu_\alpha\}}$$

- Start alternatively from mesoscopic electrolyte solution Stokes equation:

$$-\nabla p(\mathbf{r};X) + \eta_0 \Delta \mathbf{u}(\mathbf{r};X) + \rho_{el}(\mathbf{r};X)\mathbf{E}(\mathbf{r};X) = \mathbf{0} \qquad \left(\mathbf{r} \in V_{fl} \text{ and } \mathbf{E} = -\nabla\psi\right)$$

$$\Delta\psi(\mathbf{r};X) = -\frac{4\pi}{\varepsilon}\rho_{el}(\mathbf{r};X) \qquad \left(\mathbf{r} \in V_{fl}\right)$$

total **local** electric field

microion mean charge density

- Introduce hydrodynamic and Maxwell fluid stress tensors (no electrostriction)

- Hydrodynamic and Maxwell fluid stress tensors of incompressible electrolyte fluid

$$\boldsymbol{\sigma}^{h}(\mathbf{r}) = -p(\mathbf{r})\mathbf{1} + \eta_0\left[\nabla\mathbf{u} + (\nabla\mathbf{u})^{T}\right] \qquad \sigma^{h}_{\alpha\beta}(\mathbf{r}) = -p(\mathbf{r})\delta_{\alpha\beta} + \eta_0\left[\partial_\alpha u_\beta(\mathbf{r}) + \partial_\beta u_\alpha(\mathbf{r})\right]$$

$$\boldsymbol{\sigma}^{el}(\mathbf{r}) = \frac{\varepsilon}{4\pi}\left[\mathbf{E}\mathbf{E} - \frac{1}{2}|\mathbf{E}|^2\,\mathbf{1}\right] \qquad \sigma^{el}_{\alpha\beta}(\mathbf{r}) = \frac{\varepsilon}{4\pi}\left[E_\alpha(\mathbf{r})E_\beta(\mathbf{r}) - \frac{1}{2}|\mathbf{E}(\mathbf{r})|^2\,\delta_{\alpha\beta}\right]$$

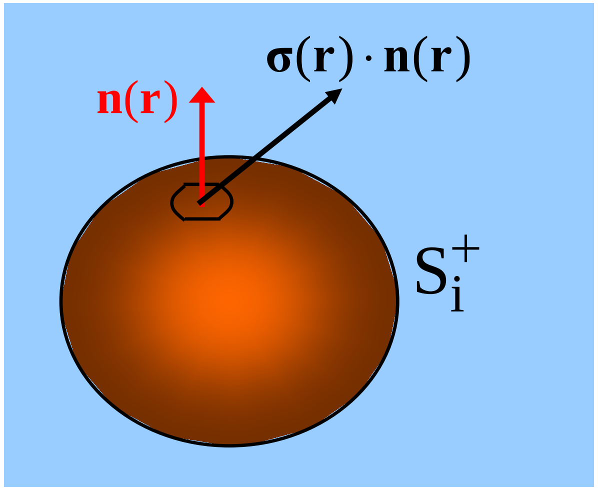
$$\nabla\cdot\left[\boldsymbol{\sigma}^{h}(\mathbf{r}) + \boldsymbol{\sigma}^{el}(\mathbf{r})\right] = -\nabla p(\mathbf{r}) + \eta_0\,\Delta\mathbf{u}(\mathbf{r}) + \rho_{el}(\mathbf{r})\mathbf{E}(\mathbf{r}) = \mathbf{0}$$

- Stokes equation

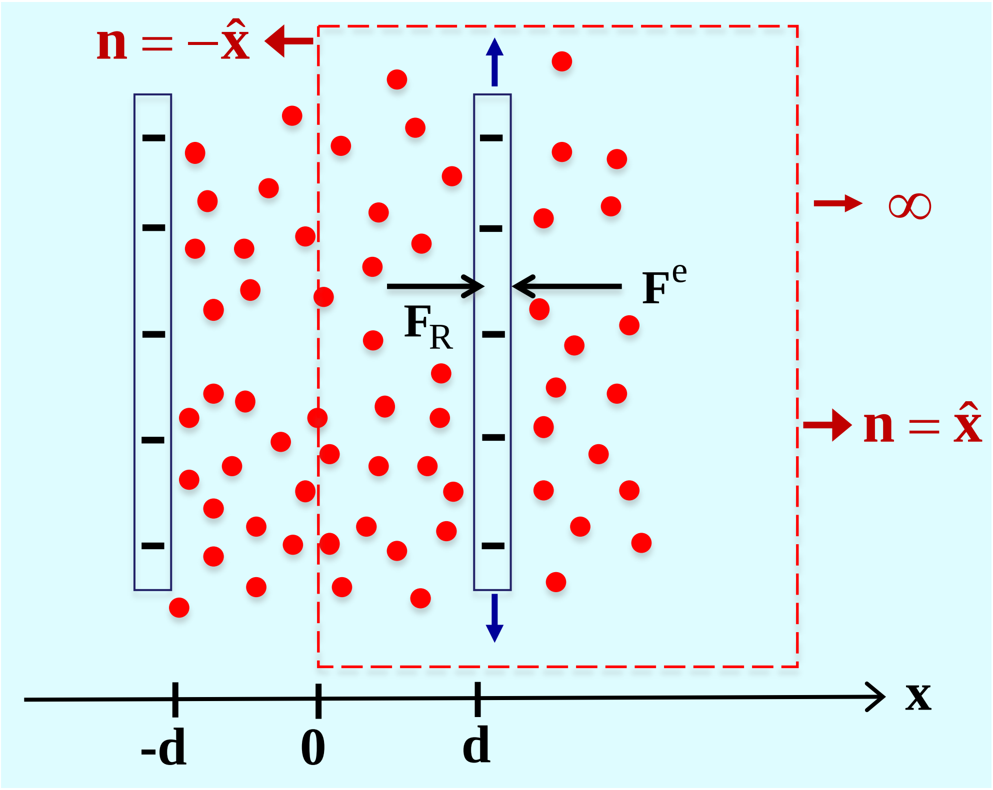
$$\boldsymbol{\sigma}(\mathbf{r}) = \boldsymbol{\sigma}^{h}(\mathbf{r}) + \boldsymbol{\sigma}^{el}(\mathbf{r})$$

$$\mathbf{F}^{T} = \int_{S_i^+} dS\,\underbrace{\boldsymbol{\sigma}(\mathbf{r};X)\cdot\mathbf{n}(\mathbf{r})} = \int_{S_i^*} dS\,\boldsymbol{\sigma}(\mathbf{r};X)\cdot\mathbf{n}(\mathbf{r}) = -\mathbf{F}^{e}$$

fluid force / area **on** sphere surface element dS
at **r** exerted by surrounding **charged** fluid



Force between two symmetric plates at static equilibrium ($\mathbf{u} = 0$)



- $\mathbf{E}(x) = -\psi'(x)\hat{\mathbf{x}}$
- $\mathbf{E}(0) = \mathbf{0}$ (EN)
- $\mathbf{F}_R = F_R\,\hat{\mathbf{x}} = -\mathbf{F}^e = -\mathbf{F}_L$

$$\hat{\mathbf{x}} \cdot \boldsymbol{\sigma}(x) \cdot \hat{\mathbf{x}} = -p(x) + \frac{\varepsilon}{8\pi}\psi'(x)^2$$

$$\frac{F_R}{A} = -\sigma_{xx}(x) + \sigma_{xx}^{res} = \left(p(x) - \frac{\varepsilon}{8\pi}\psi'(x)^2\right) - p_{res}$$

- For 1-dim. geometry only follows indeed from **static** Stokes and Poisson eqs:

$$p(x) - \frac{\varepsilon}{8\pi}E(x)^2 = \text{const}$$

Sum of **hydrostatic** (**osmotic**) and **Maxwell** pressures is constant inside two plates = static equilibrium,

- Hydrostatic pressure p in 3D PB approximation:

$$-\nabla p-\underbrace{\left(\sum_\alpha z_\alpha e\, n_\alpha^\infty \exp\{-z_\alpha e\psi\}\right)}_{\rho_{el}}\nabla\psi=-\nabla\left(p-k_BT\sum_\alpha n_\alpha(\mathbf{r})\right)=0$$

$$\boxed{p(\mathbf{r})=k_BT\sum_\alpha n_\alpha(\mathbf{r})}\qquad \left(p(\mathbf{r}\to\infty)=p_{res}=k_BT\sum_\alpha n_\alpha^\infty\right)$$

- EDL force / area on right plane is midplane – reservoir osmotic pressure difference

$$\boxed{\frac{F_L}{A}=p(x=0)-p_{res}=k_BT\sum_\alpha n_\alpha^\infty\left(\exp\{-z_\alpha e\beta\psi(0)\}-1\right)=2k_BTc_s\{\cosh[\phi(0)]-1\}}$$

- Solution of linearized PB equation for q - q electrolyte for 0 < x < h/2:

$$\phi(x)=\frac{\phi_s\cosh(\kappa x)}{\sinh(\kappa h/2)}\qquad \phi'(0)=0\qquad \varepsilon\phi'(h/2)=-\varepsilon\phi_s\kappa=-4\pi\sigma\times\beta qe$$

$$\frac{F_L(h)}{A} \approx \frac{8\pi\sigma^2}{\varepsilon q^2} \exp\{-\kappa h\}$$

- provided $\kappa h = h/\lambda_D >> 1$ and $|\phi_s| \ll 1$

- Associated effective pair potential energy of two plates:

$$\frac{u(d)}{A} = -\int_{\infty}^{h} dh' \frac{F_R(h')}{A} = \frac{\Omega_{eq}(h) - \Omega_{eq}(\infty)}{A}$$

change in grand free energy of two plates system

$$\Omega_{eq}(h) - \Omega_{eq}^{res} \approx -\frac{1}{2qe}\left[\sigma_L \phi(-h/2) + \sigma_R \phi(h/2)\right]$$

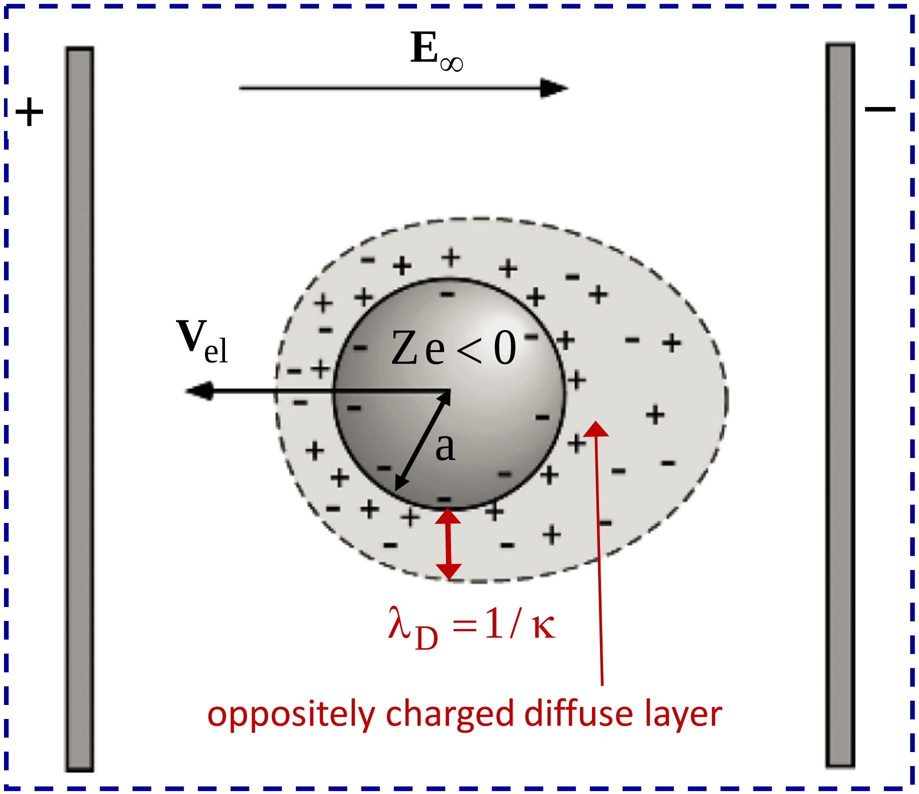
in linearized PB approximation for q - q electrolyte

4. Electrophoresis of macroions

- Hückel and Smoluchowski limits
- Henry formula
- Strongly charged macroion
- Extension to concentrated systems

4.1 Hückel and Smoluchowski limits

Non - conducting sphere with constant uniform surface potential or charge in electrolyte solution and exposed to constant external electric field



$$\mathbf{V}_{el} = \mu_{el}\,\mathbf{E}_\infty + O\left(|\mathbf{E}_\infty|^2\right)$$

- Hückel limit $\kappa a \ll 1$

$$\mathrm{F}_{el}^0 + \mathrm{F}_h^0 = Ze\,\mathrm{E}_\infty - 6\pi\eta_0 a \mathrm{V}_{el}^0 = 0$$

$$\mu_{el}^0 = \frac{Ze}{6\pi\eta_0 a}$$

- electrokinetic effects for non-dilute diffuse layer only

- Retarding **electro-osmotic drag** by cross-streaming of oppositely charged fluid near sphere surface
- Retarding **relaxation effect** force due to distortion of EDL away from spherical symmetry. Restructuring by microion diffusion and conduction, and by solvent convection is non-instantaneous

Unperturbed spherical equilibrium EDL

- Non-linear PB boundary value problem for infinite q-q electrolyte

$$\Delta\phi(r) = \phi''(r) + 2\phi'(r)/r = \kappa^2 \sinh(\phi(r)), \quad \phi(r) = \beta q e \psi(r) \quad \kappa^2 = 8\pi L_B c_s q^2$$

$$\phi'(a) = -E(a) = -L_B \frac{Zq}{a^2} \qquad \phi(r \to \infty) = 0 = \phi'(r \to \infty)$$

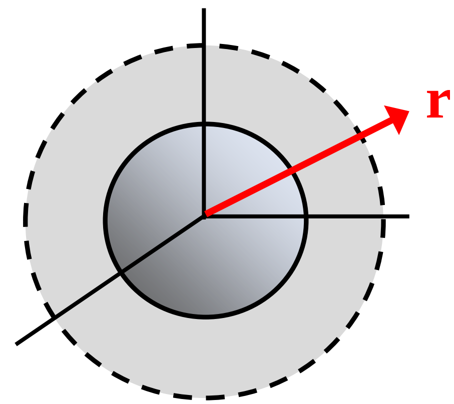
- Coulomb potential for $\kappa a \to 0$

$$\psi(r \geq a) = \frac{Ze}{\varepsilon r} = \frac{a\psi_s}{r} \qquad \psi_s = \psi(a) = \frac{Ze}{\varepsilon a}$$

$$\mu_{el}^0 = \frac{\varepsilon\zeta}{6\pi\eta_0}$$

size –indep. Hückel mobility

linear in zeta potential identified as $\zeta = \psi_s$

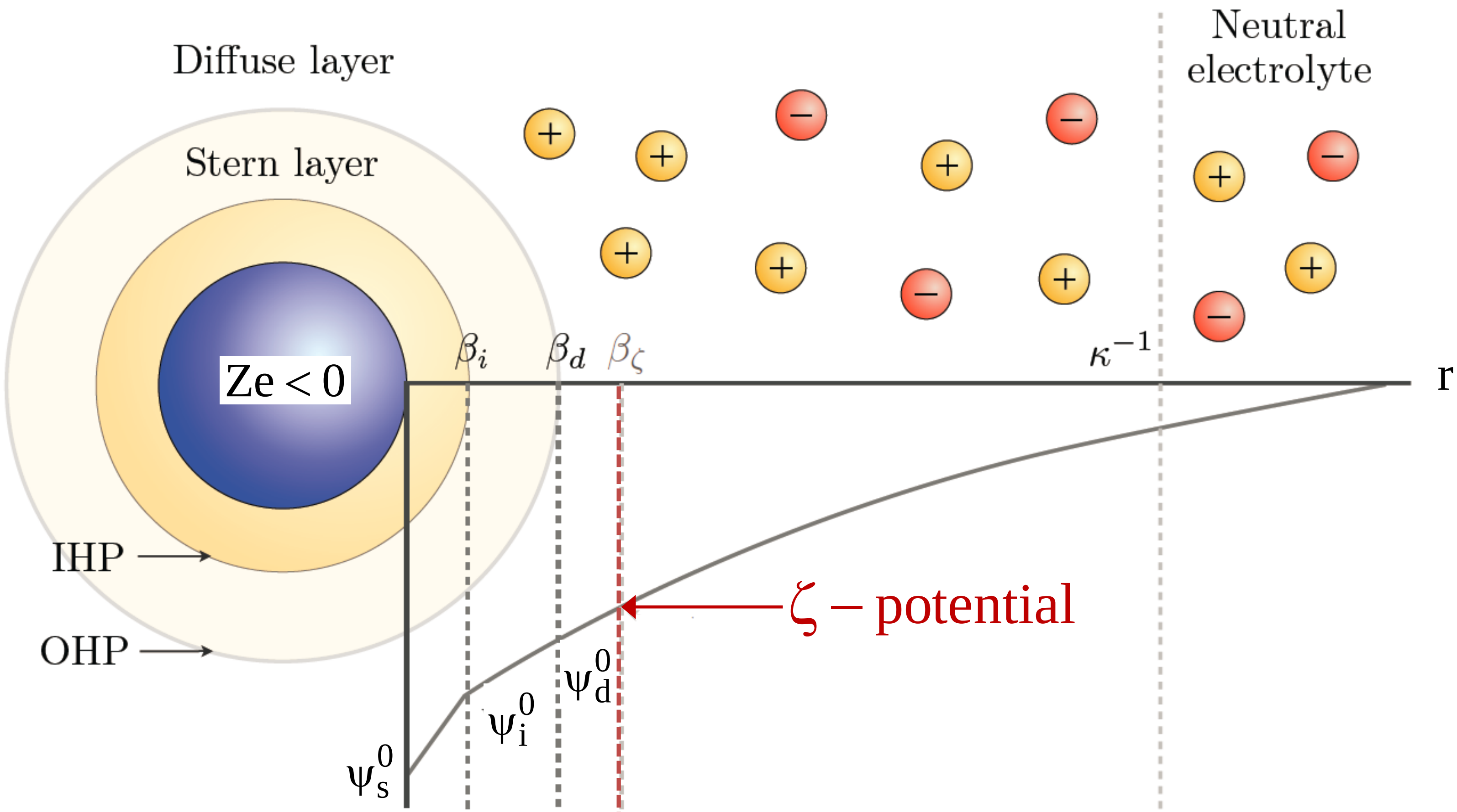


- Long-distance exponential decay for $\kappa a > 0$:

$$\Delta\psi(r \to "\infty") \sim \kappa^2 \psi(r)$$

$$\psi(r \to "\infty") \sim A \exp\{-\kappa r\}/r$$ factor $A(\kappa a, LBZq/a)$ comes from numerical solution

Helmholtz planes and zeta potential



- Zeta potential = EDL potential at zero shear surface where fluid starts to move relative to particle surface

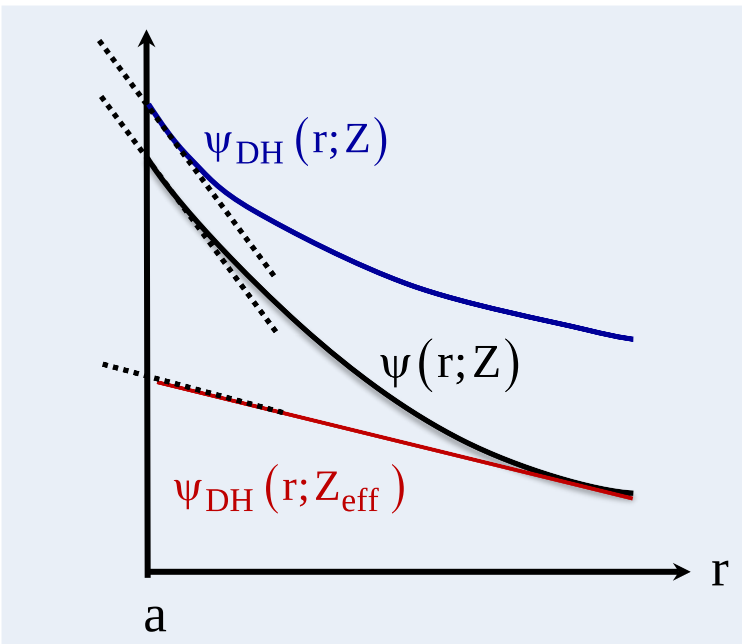
Courtesy: Rafael Roa, ICS-3, Jülich

Debye – Hückel equilibrium EDL

- Linearization is everywhere allowed only if $|L_B Zq/a| \ll 1$. One can then use inner BC:

$$\psi_{DH}(r \geq a; Z) = a\,\psi_s \frac{\exp\{-\kappa(r-a)\}}{r} = \left(\frac{Ze}{1+\kappa a}\right)\frac{\exp\{-\kappa(r-a)\}}{\varepsilon r}$$

$$Ze = \varepsilon a(1+\kappa a)\psi_s + O(\psi_s^2) \qquad \rho_{el}^{DH}(r) = -\frac{\varepsilon\kappa^2}{4\pi}\psi_{DH}(r)$$



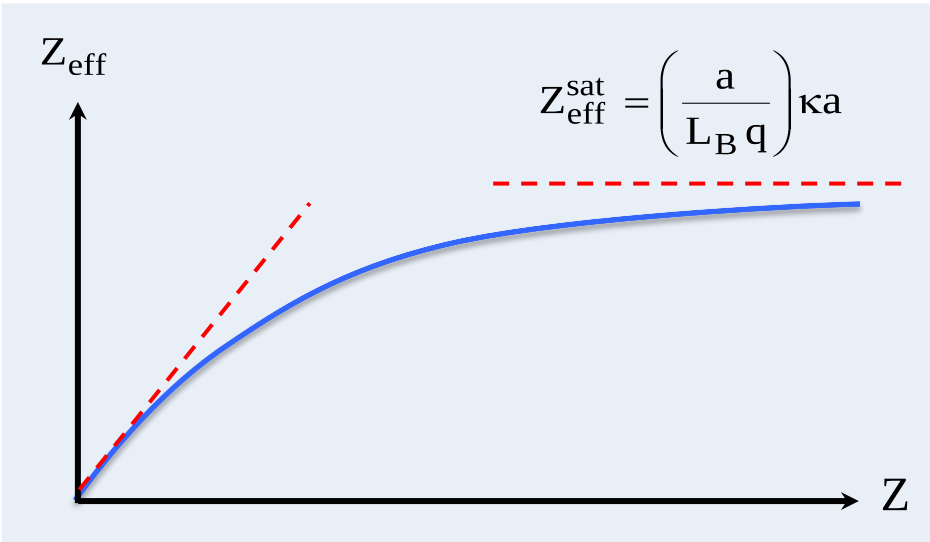
$$\psi'(a) = -\text{charge}/\left(\varepsilon a^2\right)$$

- DH overestimates strength of electric repulsion
- Effective macroion charge from long-distance matching (all derivatives)

$$Z_{eff} \leq Z$$

Analytic example: ultra - thin EDL

- Can use analytic 1-dim flat plane solution:



$$\phi_s^{sat} = \phi\left(r = a; Z \to \infty\right) = 4$$

$$n_{c-ions}^{sat} = n_{c-ions}(r = a; Z \to \infty) = \infty$$

non - physical

$$\frac{L_B q}{a} Z_{eff}(\kappa a \gg 1) = 4(\kappa a)\tanh\left\{\frac{1}{2}\,\mathrm{ar\,sinh}\left[\frac{(L_B q / a) Z}{2\kappa a}\right]\right\}$$

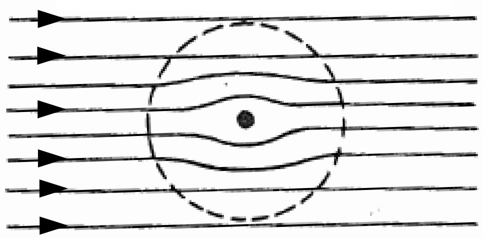
$$Z_{eff}^{sat}(\phi = 0; \kappa a > 1) = \frac{a}{L_B q}\left[6 + 4\kappa a + O\left(\frac{1}{\kappa a}\right)\right]$$

- Effective macroion charge saturation is a mean-field feature for uncorrelated point-like (monovalent) microions. It fails when microion steric effects matter.

Smoluchowski limit and flat plane electro-osmosis

Hückel limit (1920's)

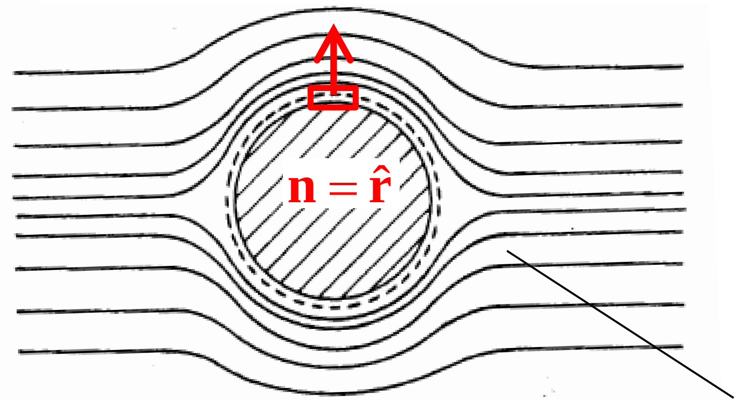
$\mathbf{E}_\infty = \text{const}$



$\kappa a \ll 1,\ \lambda_D \gg a$

- field within EDL basically undistorted

Helmholtz – Smoluchowski limit (1879 & 1903)



$\mathbf{E}_0(\mathbf{r})$

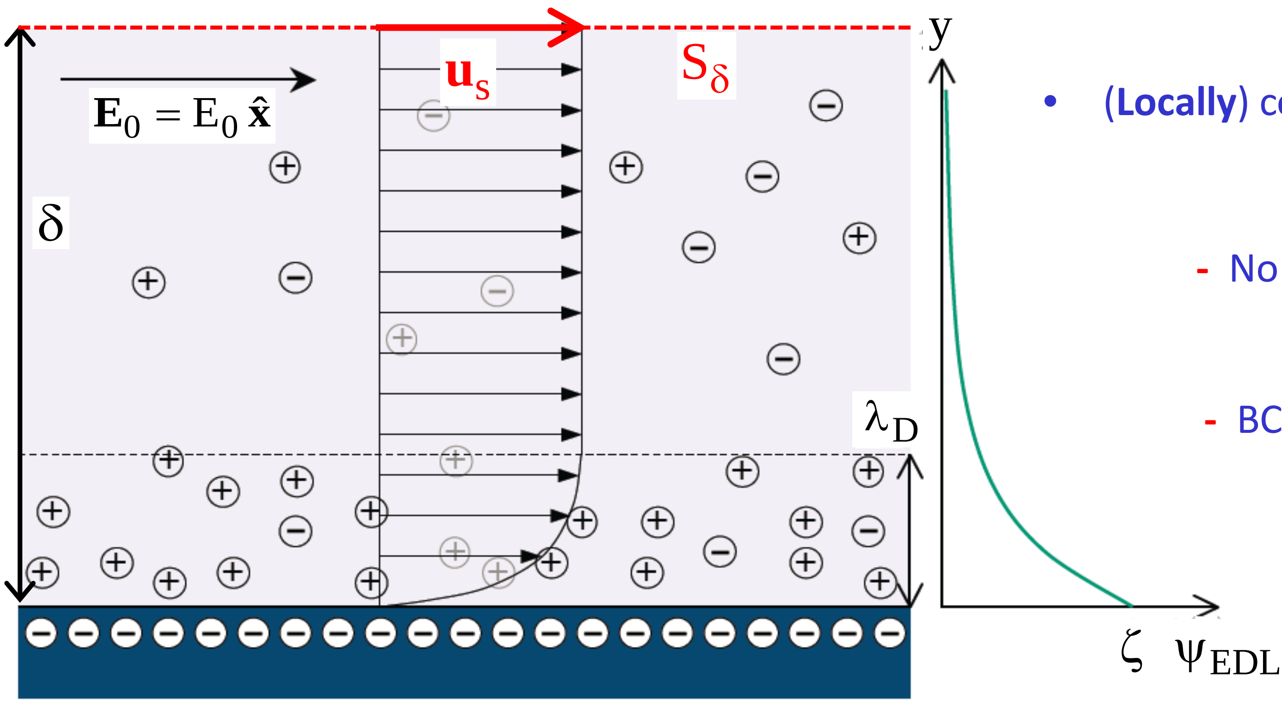
$\kappa a \gg 1,\ \lambda_D \ll a$

- field within ultrathin EDL **tangentially curved around** non – conducting sphere

$$\mathbf{E}_0(\mathbf{r} \in \text{EDL}) \propto (\mathbf{1} - \mathbf{n}\,\mathbf{n}) \cdot \mathbf{E}_\infty$$

- Electro-osmosis: flow of charged electrolyte fluid past stationary (particle) surface

- Apply Stokes equation with el. body force **inside** ulltrathin EDL. All vectors aligned with x – axis



- (**Locally**) constant incident electric field

$$\Phi_0(x) = -x\,E_0$$

- No external pressure gradient

$$\nabla p = \mathbf{0}$$

- BCs outside EDL

$$\psi_{EDL} = 0 = \psi'_{EDL} \quad (y \to \infty)$$

$$\nabla \mathbf{u}(y \to \infty) = \mathbf{0}$$

$$-\eta_0\,\Delta\mathbf{u}(y) - \nabla p(y) + \rho_{el}(y)\,\mathbf{E}_0 = \mathbf{0} \qquad \rho_{el}(y) = -\frac{\varepsilon}{4\pi}\Delta\left[\psi_{EDL}(y) + \Phi_0\right] = -\frac{\varepsilon}{4\pi}\Delta\psi_{EDL}(y)$$

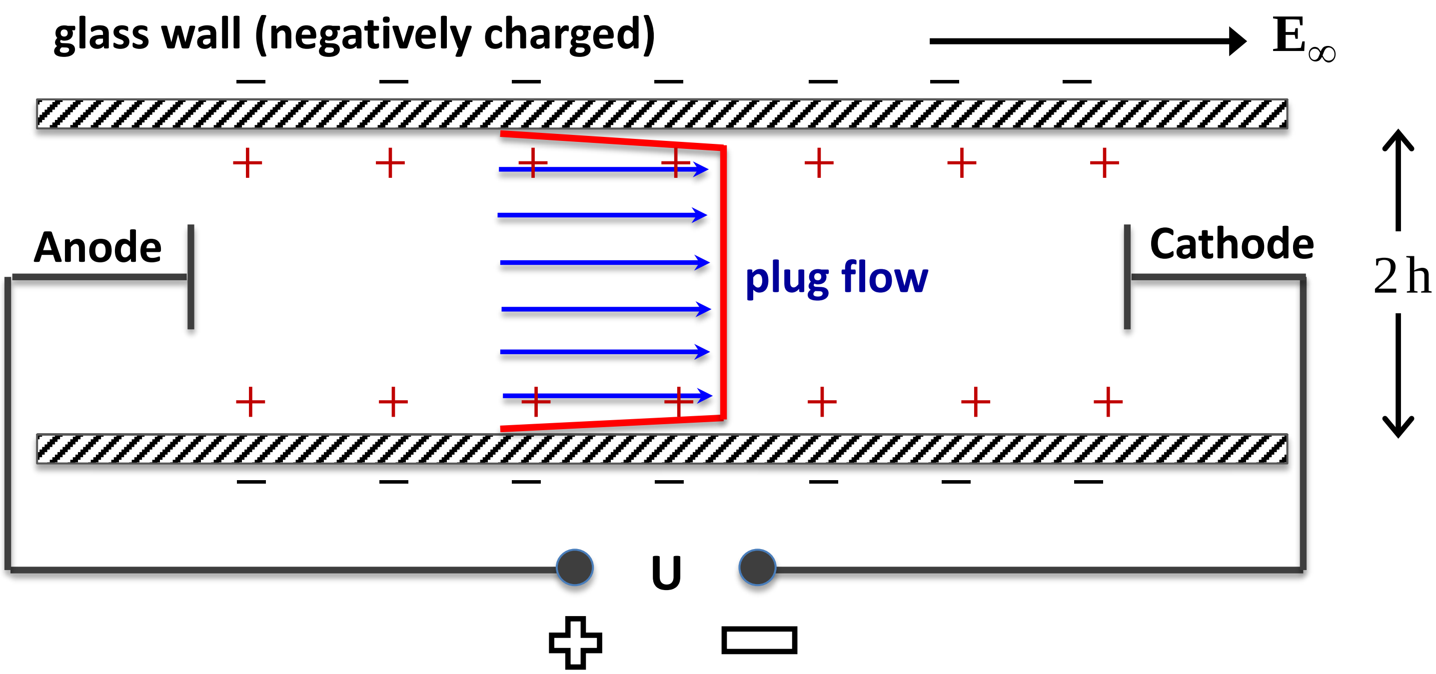
$$\Delta\left[\mathbf{u}(y) + \frac{\varepsilon\,\psi_{EDL}(y)}{4\pi\eta_0}\,\mathbf{E}_0\right] = \mathbf{0} \quad \Rightarrow \quad \mathbf{u}(y) = -\frac{\varepsilon}{4\pi\eta_0}\left[\zeta - \psi_{EDL}(y)\right]\mathbf{E}_0 \qquad \mathbf{u}(y=0) = \mathbf{0}$$

- On length scales $\gg \lambda_D$:

$$\boxed{\mathbf{u}_s = \mathbf{u}(y \gg \lambda_D) = -\frac{\varepsilon\,\zeta}{4\pi\eta_0}\,\mathbf{E}_0}$$

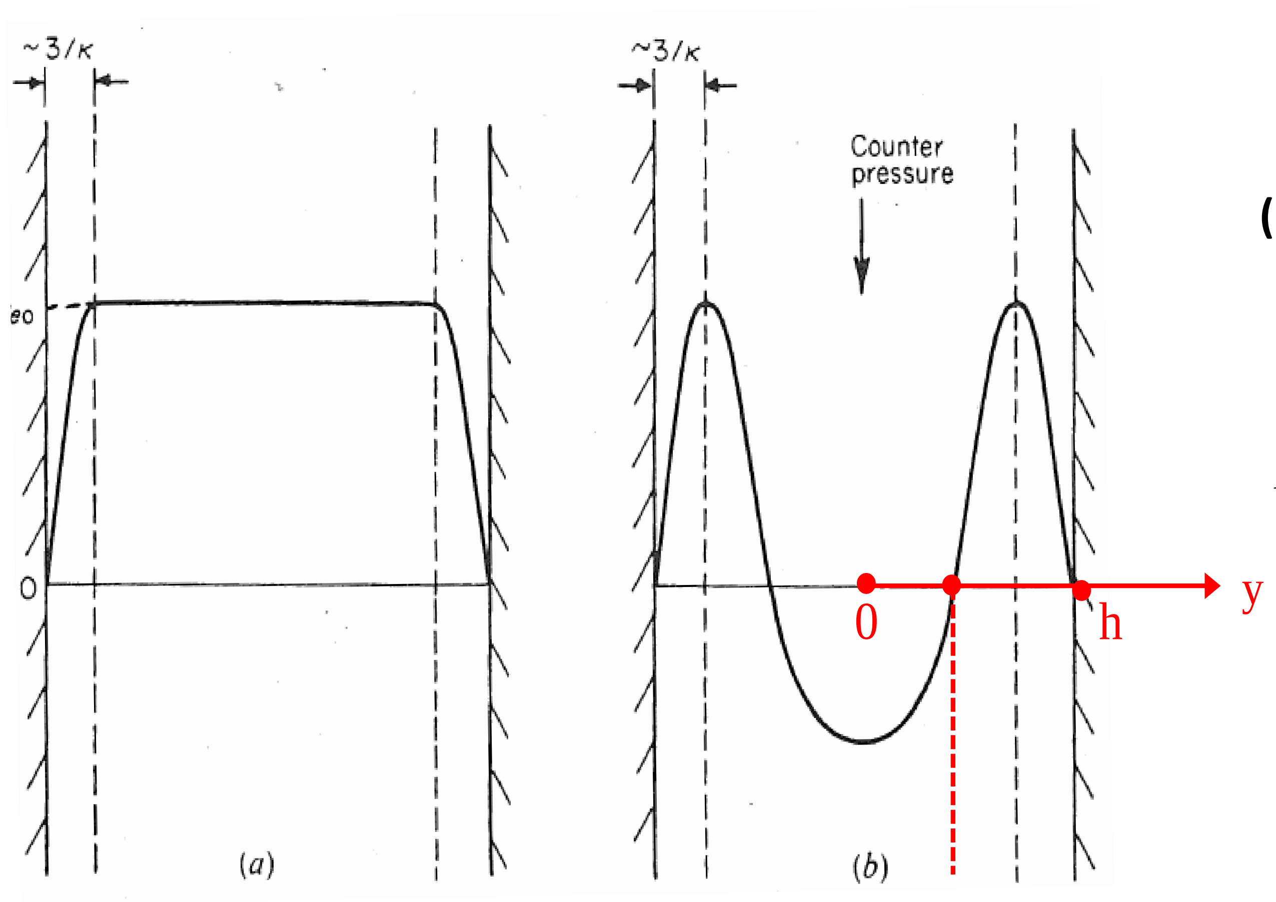
effective slip velocity (flat plate rest frame)

Electro - osmotic plug flow in an open capillary tube



- Electroosmosis used in microfluid devices to drive aqueous media through narrow micro - channels where Low-Reynolds number fluid dynamics applies to

Open (a) versus closed (b) electro-osmotic cells



$h/\sqrt{3}$ if $\kappa h \gg 1$

Sketch
(not to scale)

$$\int_A dS\,\mathbf{u} = \mathbf{0}$$

- Absolute electrophoretic velocity measured in zero flow plane (Malvern Zeta-sizer)

Electro - flow problem outside thin EDL: matched asymptotic expansion

- Stokes equation w/o body force ($\varrho_{el} = 0$) and slip inner velocity BC. Laplace equation for Φ_0
- Spherical surface S_δ of radius a + δ with $\delta \gg \lambda D$

$$-\eta_0 \Delta \mathbf{u}(\mathbf{r}) - \nabla p(\mathbf{r}) = \mathbf{0}, \quad \nabla \cdot \mathbf{u} = 0$$

$$\mathbf{u} = \mathbf{u}_s + \mathbf{V}_{el} + \mathbf{\Omega}_{el} \times \mathbf{r} \quad \text{on } S_\delta$$

$$\mathbf{u} \to \mathbf{0} \quad \text{for } |\mathbf{r}| \to 0$$ Lab rest frame

- Zero electric force / torque on sphere + EDL:

$$\mathbf{F}^T = \int_{S_\delta} dS\, \boldsymbol{\sigma}^h \cdot \mathbf{n} = \mathbf{0}$$

$$\mathbf{T}^T = \int_{S_\delta} dS\, \mathbf{r} \times \left(\boldsymbol{\sigma}^h \cdot \mathbf{n}\right) = \mathbf{0}$$

$\Longrightarrow$

$$\mathbf{u} \to O\left(\frac{1}{r^2}\right) \quad \text{at least, for } |\mathbf{r}| \to 0$$

$$\Delta \Phi_0(\mathbf{r}) = \mathbf{0}$$ (source of Φ_0 is source of $\mathbf{E}_\infty$)

$$\mathbf{n} \cdot \nabla \Phi_0(\mathbf{r}) = \mathbf{0} \quad \text{on } S_\delta$$

$$\nabla \Phi_0(\mathbf{r}) \to -\mathbf{E}_\infty \quad \text{for } |\mathbf{r}| \to \infty$$

Neutral & non-conducting sphere

$\Longrightarrow$

$$\mathbf{E}_0(\mathbf{r}) = \left[1 + \frac{1}{2}\left(\frac{a}{r}\right)^3 (1 - 3\hat{\mathbf{r}}\hat{\mathbf{r}})\right] \cdot \mathbf{E}_\infty$$

$$\mathbf{E}_s \approx \mathbf{E}_0(\mathbf{r} = a\hat{\mathbf{r}}) = \frac{3}{2}(1 - \hat{\mathbf{r}}\hat{\mathbf{r}}) \cdot \mathbf{E}_\infty \perp \hat{\mathbf{r}}$$

$$\boxed{\mathbf{u}_s = -\frac{3\varepsilon\,\zeta}{8\pi}(\mathbf{1} - \hat{\mathbf{r}}\hat{\mathbf{r}}) \cdot \mathbf{E}_\infty}$$ BC on S_δ

- Inspired guess: assume that outer flow field is given by „extension of BC on S_δ

$$\mathbf{u}(\mathbf{r}) = -\frac{\varepsilon\zeta}{4\pi\eta_0}\mathbf{E}_0(\mathbf{r}) + \mathbf{V}_{el} \quad (r > a + \delta)$$

irrotational potential flow ansatz

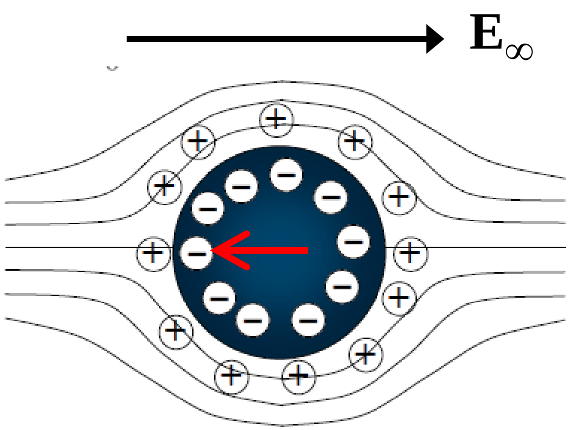
Check if ok: $\Delta\mathbf{u} = \frac{\varepsilon\zeta}{4\pi\eta_0}\nabla(\Delta\Phi_0) = \mathbf{0} \;\Rightarrow\; \nabla p = \mathbf{0}$ constant pressure

$$\nabla\cdot\mathbf{u} = \frac{\varepsilon\zeta}{4\pi\eta_0}\Delta\Phi_0 = 0 \qquad \mathbf{u}(\mathbf{r}\to"\infty") = O\left(\frac{1}{r^3}\right)$$

This is **unique** solution of outer BVP, giving the electrophoretic velocity for fixed zeta potential:

$$\mathbf{V}_{el}^{Sm} = \frac{\varepsilon\zeta}{4\pi\eta_0}\mathbf{E}_0(\mathbf{r}\to\infty) = \frac{\varepsilon\zeta}{4\pi\eta_0}\mathbf{E}_\infty$$

$$\mu_{el}^{Sm} = \frac{\varepsilon\zeta}{4\pi\eta_0} = \frac{3}{2}\mu_{el}^{0}$$



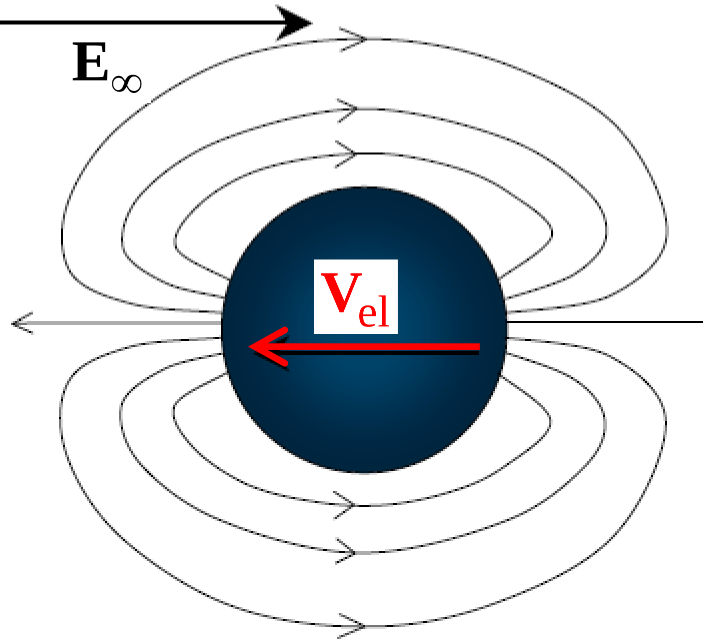
- Tangential electric field strength at S is $1.5 \times E_\infty$

Streamlines of dipolar potential flow outside the EDL

$$\mathbf{u}(\mathbf{r}) = -\mu_{el}^{Sm}\left[\mathbf{E}_\infty - \mathbf{E}_0(\mathbf{r})\right] \quad (r > a + \delta)$$

$$\mathbf{u}(\mathbf{r}) = -\mu_{el}^{Sm}\frac{1}{2}\left(\frac{a}{r}\right)^3\left[\mathbf{1} - 3\hat{\mathbf{r}}\hat{\mathbf{r}}\right]\cdot\mathbf{E}_\infty = -\nabla\Psi_p(\mathbf{r})$$

$$\Psi_p(\mathbf{r}) = \frac{\mu_{el}^{Sm}}{2}\left(\frac{a}{r}\right)^3 \mathbf{r}\cdot\mathbf{E}_\infty$$

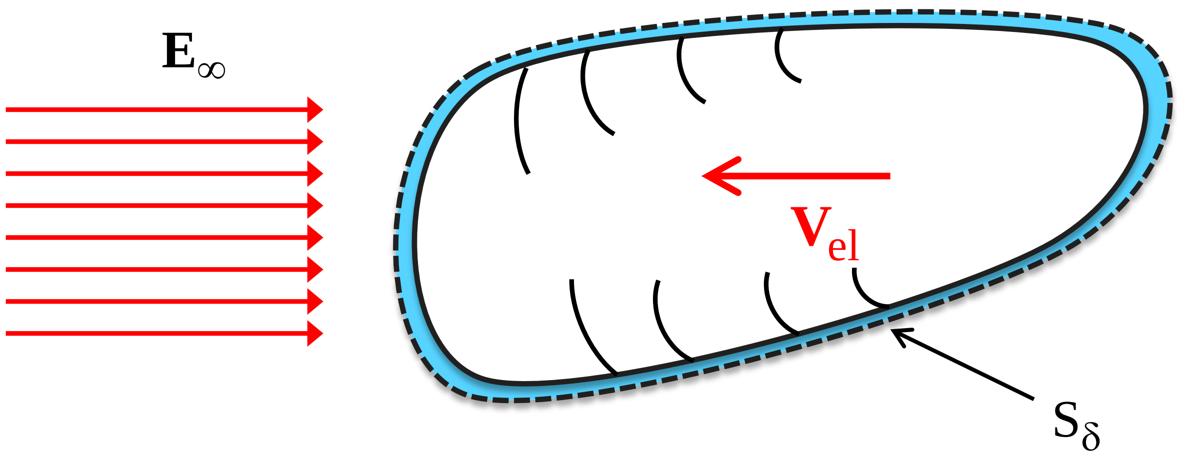


$$\nabla \times \mathbf{u} = \mathbf{0}$$

- Flow decays faster than the hydrodynamic Stokes dipole of an active swimmer

Electrophoresis of arbitrarily shaped rigid macroion with ultrathin EDL

$$\mathbf{V}_{\mathrm{el}}^{\mathrm{Sm}} = \frac{\varepsilon\zeta}{4\pi\eta_0}\mathbf{E}_\infty , \quad \boldsymbol{\Omega}_{\mathrm{el}}^{\mathrm{Sm}} = \mathbf{0}$$



- Smooth surface with curvature radii everywhere $\gg \lambda_D$
- **Constant surface (i.e. zeta) potential**
- No perpendicular charge conduction inside thin diffuse layer
- External el. field homogeneous on size scale of macroion
- PB – based mean-field result

- Outside BV part:

$$\Delta\mathbf{u}(\mathbf{r}) = \mathbf{0}$$

$$\mathbf{n}\cdot\mathbf{u}(\mathbf{r}) = 0 \text{ on } S_\delta$$

$$\Delta\Phi_0(\mathbf{r}) = 0$$

$$\mathbf{n}\cdot\nabla\Phi_0(\mathbf{r}) = 0 \text{ on } S_\delta$$

- Φ_0 more complex, but still:

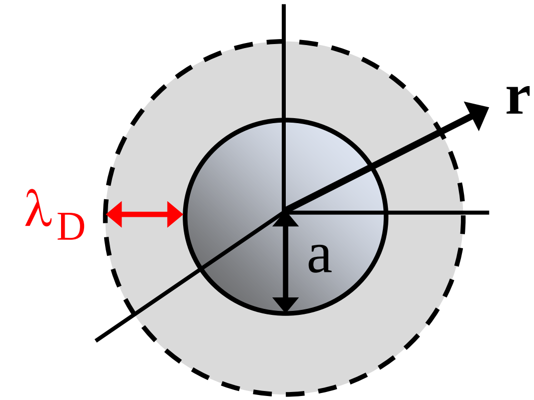
$$\mathbf{u}(\mathbf{r}) = -\mu_{\mathrm{el}}^{\mathrm{Sm}}\left[\mathbf{E}_\infty - \mathbf{E}_0(\mathbf{r})\right]$$

- shape-indep. asymptotic form

Keh & Anderson, J. Fluid Mech. 153 (1985); Teubner, J. Chem. Phys. 76 (1982)

4.2 Henry formula

- Electrophoresis of charged sphere with extended EDL



$$\mathbf{F}^{el} + \mathbf{F}^{h} = \mathbf{0}$$ macroion and fluid are inertia-free

$$\mathbf{F}^{el} = \int_{S_a} dS\, \boldsymbol{\sigma}^{el} \cdot \mathbf{n} = -\int_{V_{fl}} d^3r\, \rho_{el}\, \mathbf{E}$$ electric force on sphere = - force on diffuse layer

$$\mathbf{u}(\mathbf{r} \to \infty) = -\mathbf{V}_{el}$$

$$\mathbf{F}^{h} = 6\pi\eta_0 a \left[1 + \frac{a^2}{6}\Delta\right] \mathbf{u}_{in}(\mathbf{r} = \mathbf{0})$$ hyd. drag force on stationary neutral sphere with stick BC in incident flow field created by sources outside the sphere

$$\mathbf{u}_{in}(\mathbf{r}) = -\mathbf{V}_{el} + \int_{V_{fl}} d^3\mathbf{r}'\, \mathbf{T}^0(\mathbf{r} - \mathbf{r}') \cdot \rho_{el}(\mathbf{r}')\mathbf{E}(\mathbf{r}') \quad \Rightarrow$$

$$\boxed{6\pi\eta_0 a\, \mathbf{V}_{el} = \int_{V_{fl}} d^3r \left[\mathbf{U}^{St}(\mathbf{r}) - \mathbf{1}\right] \cdot \rho_{el}(\mathbf{r}')\mathbf{E}(\mathbf{r})}$$

$$\mathbf{U}_{St}(\mathbf{r}) = 6\pi\eta_0 a \left[1 + \frac{a^2}{6}\Delta\right] \mathbf{T}^0(\mathbf{r})$$

$\rho_{el} = -\frac{\varepsilon}{4\pi}\Delta\psi$; $\mathbf{E}$: total local electric field

$$\mathbf{E} = -\nabla\psi = -\nabla\left(\psi_{EDL} + \Phi\right) \qquad \Phi\left(\mathbf{r}\to\infty\right) = -\mathbf{r}\cdot\mathbf{E}_\infty \qquad \Phi \propto E_\infty$$

- Double linear expansion, in E_∞ and in normalized zeta potential

$$\tilde{\zeta} = \left| qe\zeta/(k_B T) \right|$$

$$\psi_{EDL} = \psi_{EDL}^{eq} + O\left(E_\infty\right) \qquad \psi_{EDL} = \psi_{EDL}^{eq,DH} + O\left(E_\infty, \tilde{\zeta}^2\right)$$

$$\Phi\left(\mathbf{r}\right) = \Phi_0\left(r\right) + O(\tilde{\zeta})$$ potential of neutral , non-conducting sphere subjected to E_∞

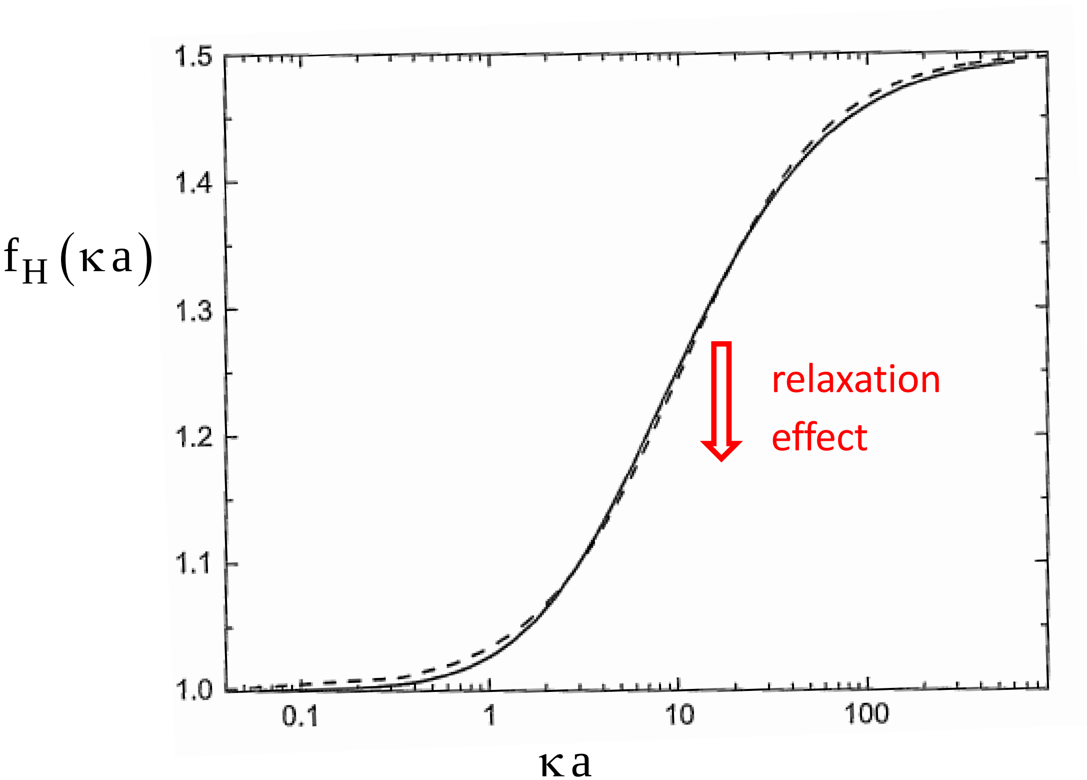
$$6\pi\eta_0 a\,\mathbf{V}_{el} = -\int_{V_{fl}} d^3r \left[\mathbf{U}^{St}\left(\mathbf{r}\right) - \mathbf{1}\right]\cdot\frac{\varepsilon}{4\pi}\underbrace{\Delta\psi_{EDL}^{eq,DH}\left(r\right)}_{\kappa^2\psi_{EDL}^{eq,DH}}\underbrace{\mathbf{E}_0\left(\mathbf{r}\right)}_{-\nabla\Phi_0} + O(E_\infty^2, \tilde{\zeta}^2)$$

- To linear order in (small) zeta potential: **no relaxation effect contribution**

- Result after integration is the Henry formula (1931)

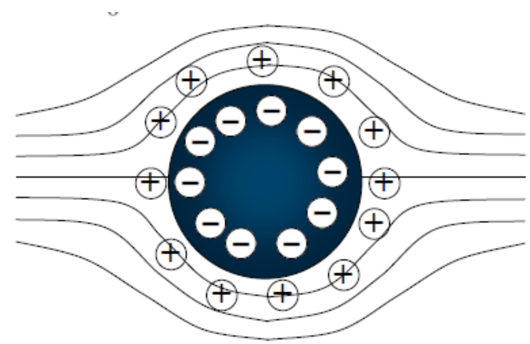
$$\mu_{el}^{H} = \frac{\varepsilon \zeta}{4\pi\eta_0} f_H(\kappa a) = \mu_{el}^{0} \times f_H(\kappa a)$$

valid for small and constant zeta potential or charge. For which DH theory applies to.



$$f_H(x) = 1 + \frac{1}{4} x^2 \exp\{x\}[E_3(x) - E_5(x)]$$

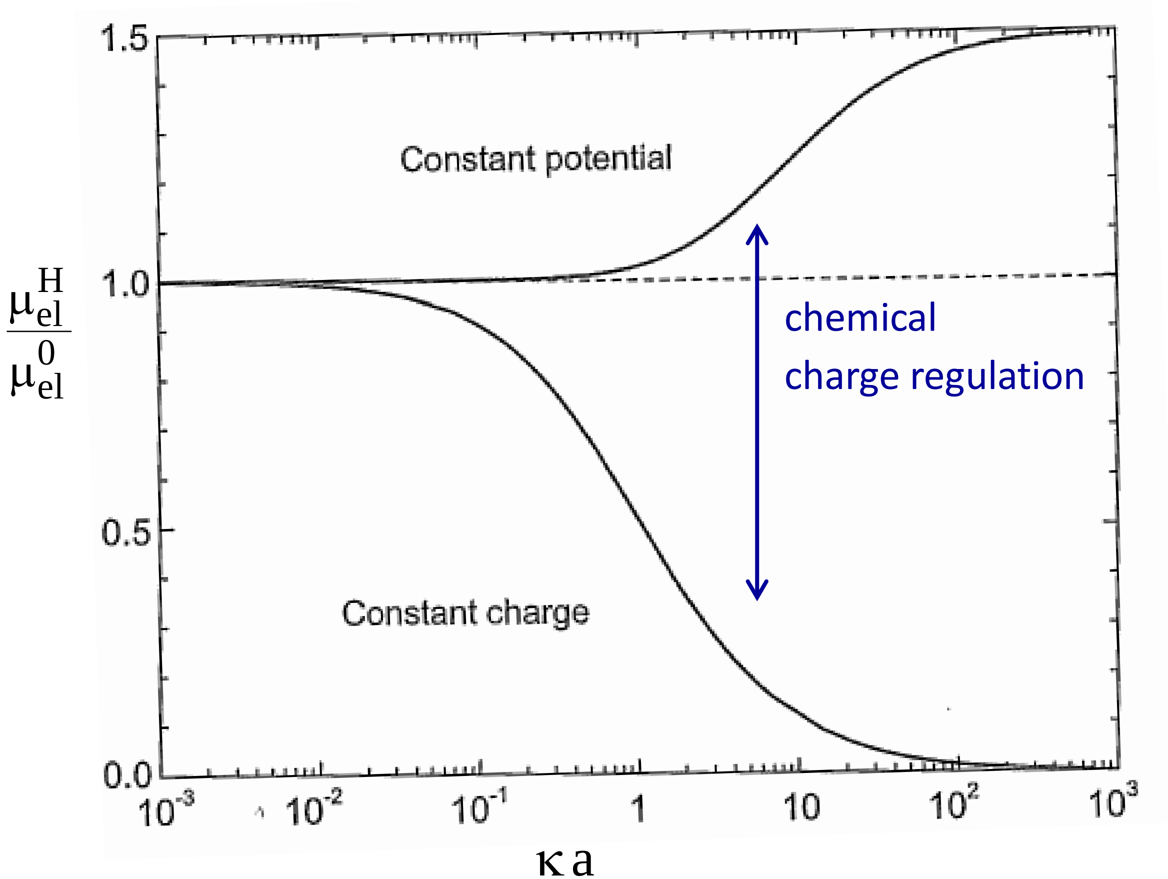
$$f_H(0) = 1 \qquad f_H(\infty) = 3/2$$



- Macroion charge increases with increasing salinity for fixed potential. The increase of the bare electric force nearly counterbalanced by increased counterion electro-osmotic flow

Constant potential versus constant surface charge electric BC

$$Ze = \varepsilon a(1+\kappa a)\psi_s + O(\psi_s^2)$$

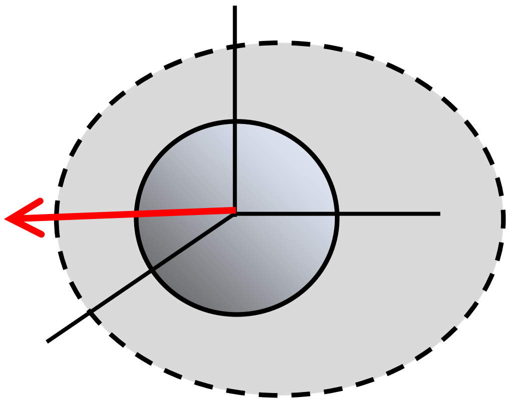


$$\mu_{el}^{H}\Big|_{\zeta} = \mu_{el}^{0} \times f_H(\kappa a)$$

$$\mu_{el}^{H}\Big|_{Z} = \mu_{el}^{0} \times \frac{f_H(\kappa a)}{1+\kappa a}$$

- Fixed macroion charge increasingly screened from external field with increasing salinity

4.3 Strongly charged macroion



- Stokes equation with electric body force
- Poisson equation for **total** mean electric potential
- Continuity equation for microion currents **(1-1 electrolyte)**:

$$(\partial / \partial t) n_\alpha = 0 = \nabla \cdot \mathbf{j}_\alpha(\mathbf{r}) \quad (\alpha = 1, 2 = \pm)$$

- Nernst-Planck MF convection - el. migration - diffusion currents:

$$\mathbf{u}(\mathbf{r} \to \infty) = -\mathbf{V}_{el}$$

$$\mathbf{j}_\pm(\mathbf{r}) = n_\pm(\mathbf{r})\mathbf{u}(\mathbf{r}) + n_\pm(\mathbf{r})\beta D_\pm^0 (\mp e \nabla \psi) - D_\pm^0 \nabla n_\pm(\mathbf{r})$$

$$\boxed{\mathbf{j}_\pm(\mathbf{r}) = n_\pm(\mathbf{r})\mathbf{u}(\mathbf{r}) - \beta D_\pm^0 n_\pm(\mathbf{r}) \nabla \mu_\pm(\mathbf{r})}$$

- relation to DDFT

$$\mu_\pm(\mathbf{r}) = \pm e \psi(\mathbf{r}) + k_B T \ln\left[\frac{n_\pm(\mathbf{r})}{n_\pm^\infty}\right]$$

- MF electro-chemical potential
- constant for zero external field; gives then PB equation for microions

$$\boxed{n_\pm(\mathbf{r}) = n_\pm^\infty \exp\{-\beta[\pm e \psi(\mathbf{r}) - \mu_\pm(\mathbf{r})]\}}$$

- outside the sphere

- All currents are zero w/o external field, and electrochemical potential is constant
- Boundary conditions:

$$\mathbf{v}_{\pm}(a\,\hat{\mathbf{r}})\cdot\mathbf{n} = 0 = \mathbf{u}(a\,\hat{\mathbf{r}})\cdot\mathbf{n}$$

- insulating and solvent-impermeable sphere

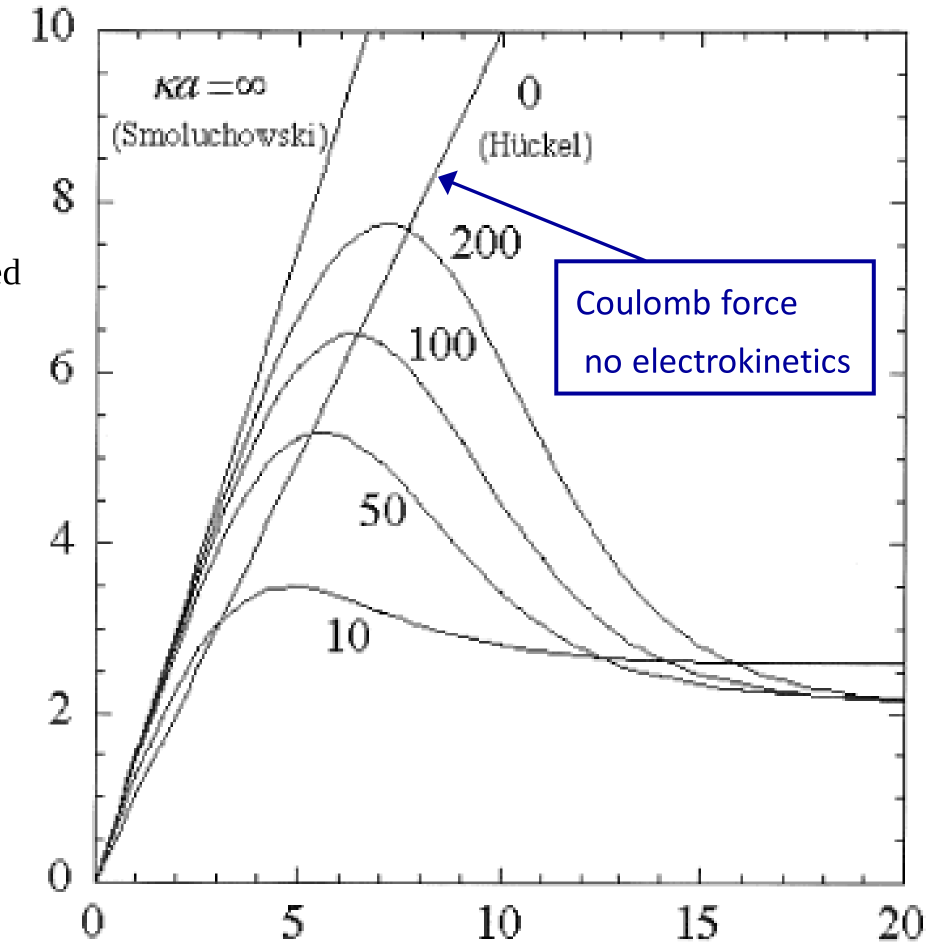
$$\Longrightarrow \quad \nabla\mu_{\pm}(a\,\hat{\mathbf{r}})\cdot\mathbf{n} = 0$$

$$n_{\pm}(\mathbf{r}\to\infty) = n_{\pm}^{\infty}$$

- also in presence of external field

$$\Longrightarrow \quad \nabla\mu_{\pm}(\mathbf{r}\to\infty) = \pm e\,\nabla\psi(\mathbf{r}\to\infty) = \mp\, e\,\mathbf{E}_{\infty}$$

- Field of electro-chemical potential (ECP) trangential to sphere surface
- ECP is independent of electric BC on sphere surface
- Expansion of all potentials and densities to linear order in external field leads to set of differential equations which can be solved numerically to obtain the el. mobility
- Ohshima provides analytic expressions valid in certain salinity ranges



μ_{el}^{red}

$\tilde{\zeta} = e\zeta/(k_B T)$

$$\mu_{el}^{red} = \frac{\mu_{el}}{\mu_{el}^{H}(a = L_B, Z = 1)}$$

$$\mu_{el}^{H}(L_B, Z = 1) = \frac{e}{6\pi\eta_0 L_B}$$

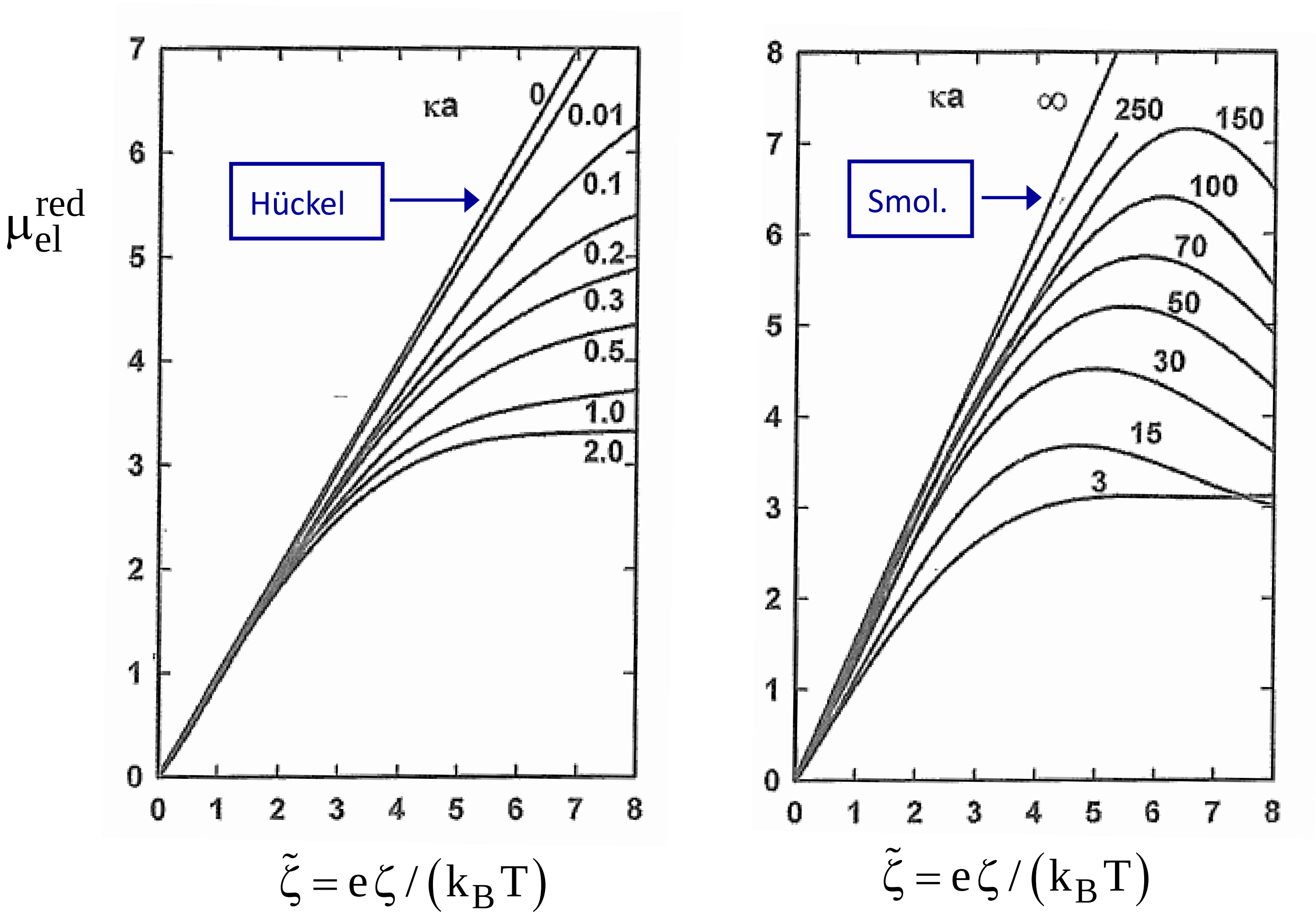
$$\mu_{red}^{el} = \begin{cases} \frac{3}{2}\tilde{\zeta} & \text{for } \kappa a \gg 1 \\ \tilde{\zeta} & \text{for } \kappa a \ll 1 \end{cases}$$

$$\mu_{el}^{red}(\kappa a \gg 1 \text{ finite}, \zeta \to \infty) = 2\log(2)$$

- Mobility maximum: inhomogeneous conduction of counterions in thin diffuse layer .

  Assoc. slowing relaxation force grows faster with zeta potential than bare Coulomb force.

H. Ohshima, „Theory of Colloida and Interfacial Phenomena“, Elsevier (2006)



- With increasing reduced zeta potential > 3, increasing salinity required to approach the Smoluchowski limit.

O'Brien and White, J. Chem. Soc. Faraday Trans. II 74 (1987)

Relaxation effect: counter - ion concentration profile and eletric dipole moment

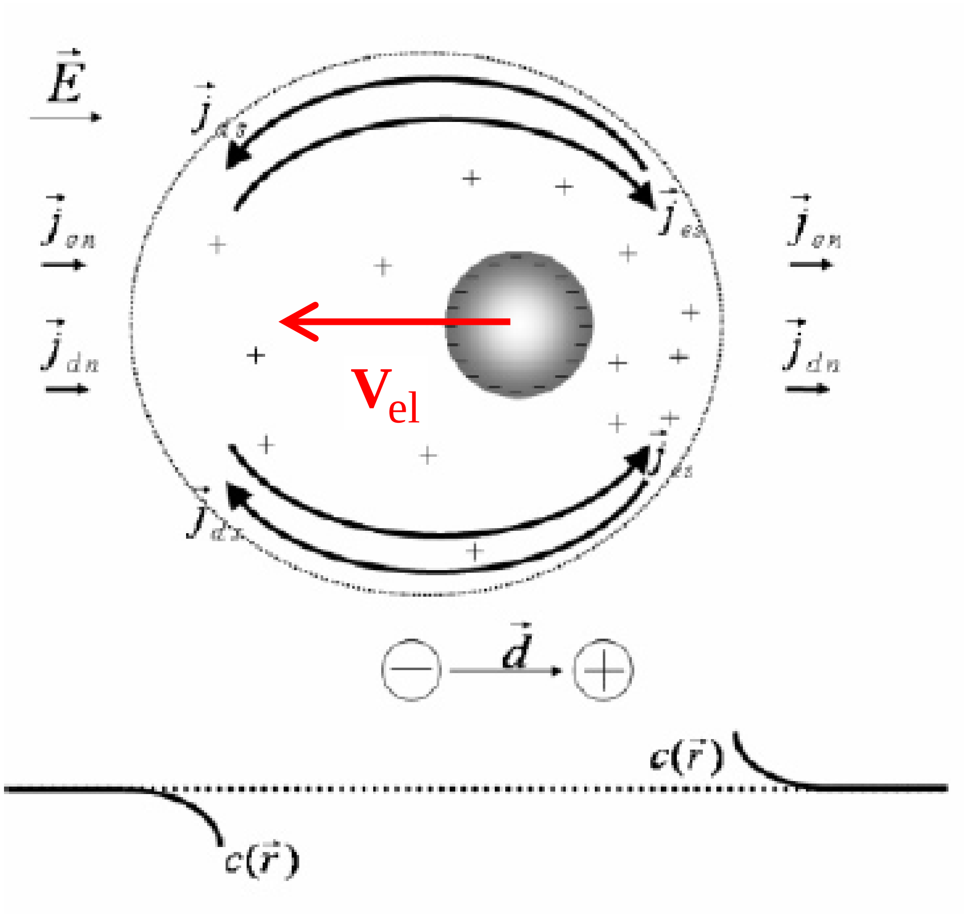
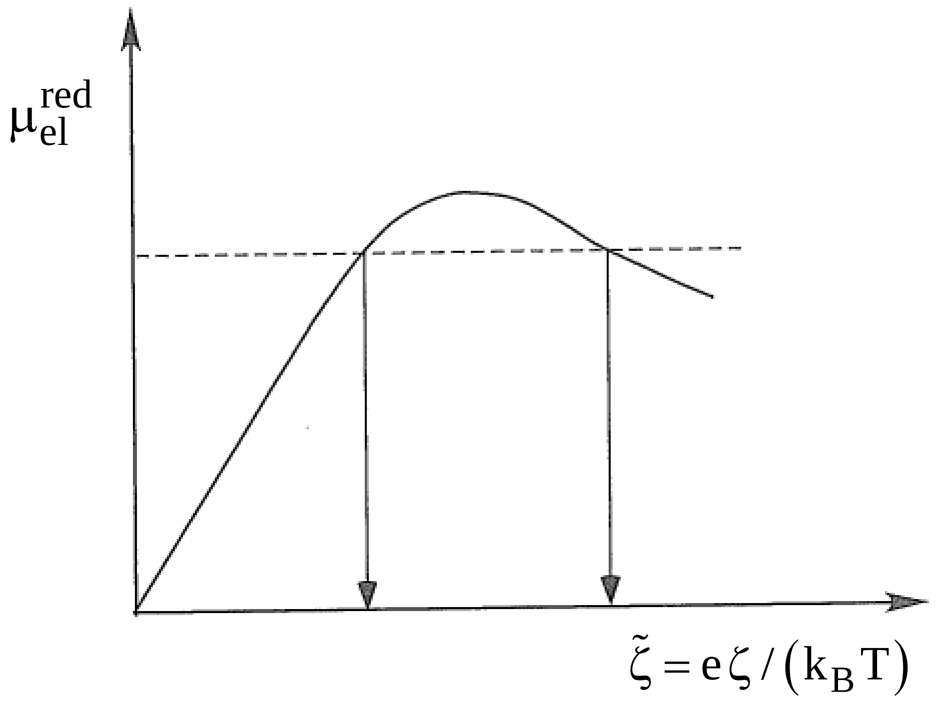


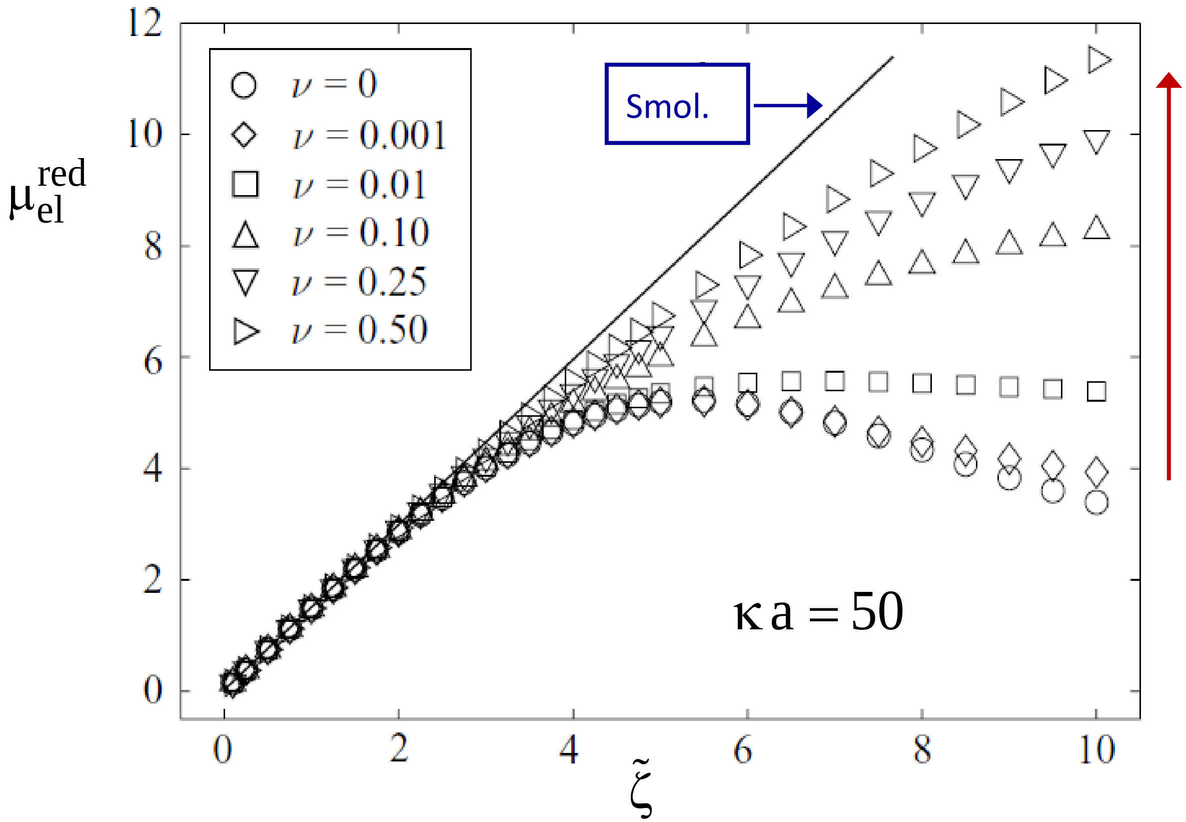
figure taken from: F. Carrique et al., Langmuir **24**, 2395 (2008)



- MF Implication: no 1 -1 correspondence between electrophoretic velocity and zeta potential

Inclusion of ion steric effects on level of activity coefficients (Bikerman)

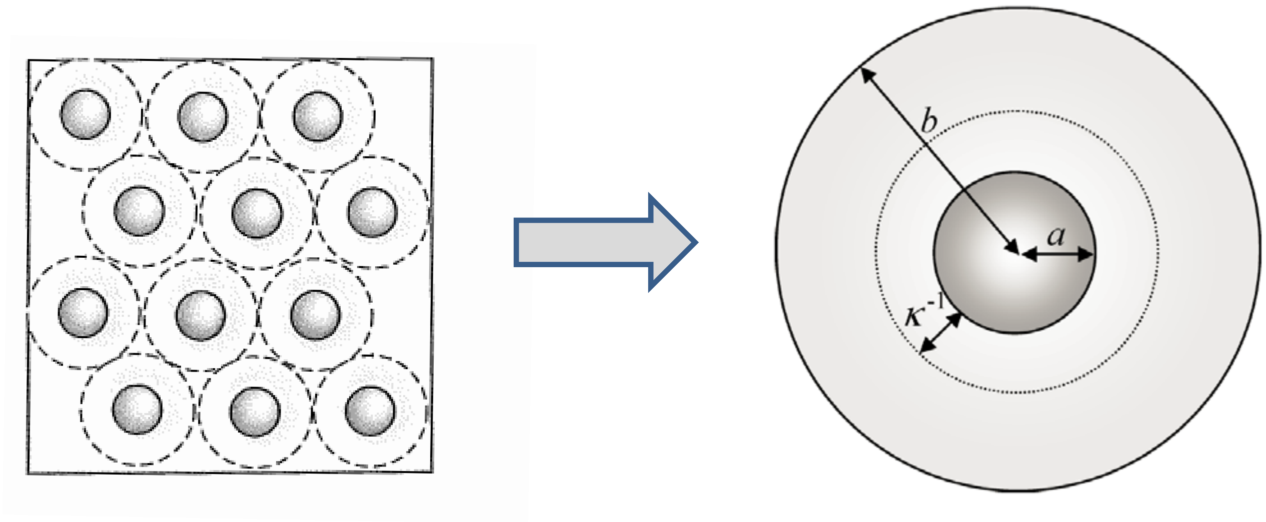
$$\mu_\pm(\mathbf{r}) = \pm e\psi(\mathbf{r}) + k_B T \ln\left[\frac{n_\pm(\mathbf{r})}{n_\pm^\infty}\right] - k_B T \ln\left[1 - n_+(\mathbf{r})a_s^3 - n_-(\mathbf{r})a_s^3\right]$$



Inceasing **microion** volume fraction ν reduces „surface conduction“

- A.S. Khair and T. Squires, J. Fluid Mech. **640**, 343 (2009)
- Poster 25 by Rafael Roa

4.4 Extension to concentrated systems



$$\phi = \left(\frac{a}{b}\right)^3$$

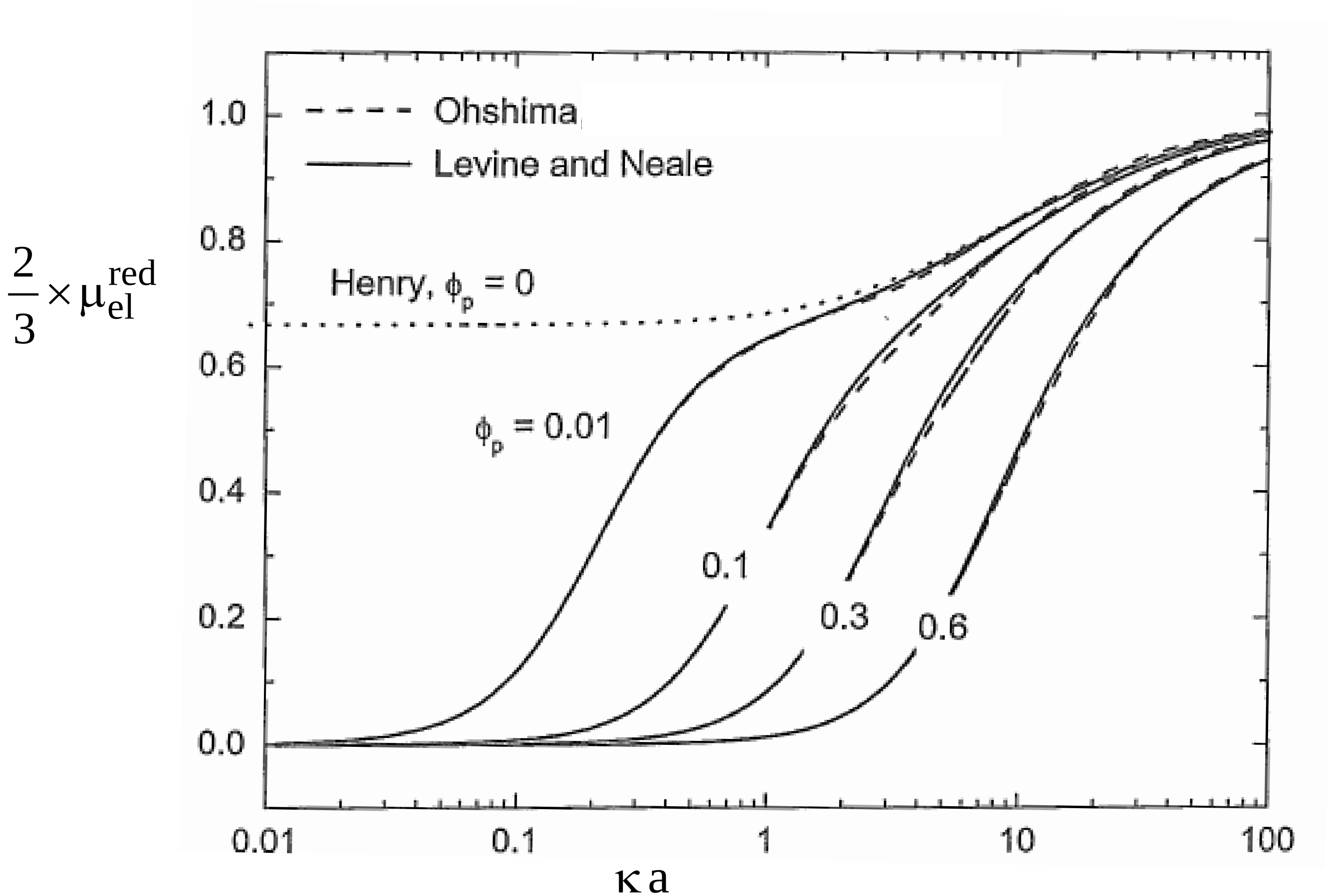
- MF elektrokinetic equations with standard inner BCs
- Specify outer BCs on outer cell boundary r = b :

1. zero vorticity (Kuwabara): $\nabla \times \mathbf{u}(\mathbf{r}) = \mathbf{0}$

   or: zero tangential hydrodynamic shear stress (Brenner)

2. unperturbed EDL field is zero at outer cell boundary (cell overall electroneutral)

Cell model extension of Henry formula (small zeta potential)



- Strong mobility reduction by electro-osmotic drag for extended EDLs and increasing colloid particles volume fraction
- For larger (fixed) zeta potential: mobility decreases with increasing volume fraction

Levine and Neal, JCIS **47** (1974); Ohshima, JCIS **188** (1997)

Principal drawbacks of the cell model (despite its success in exp. applications):

- It disregards fluid-like near-field ordering of the colloids
- Selection of outer BCs is to some extent arbitrary
- Wrong low - concentration prediction. The correct one is for $\kappa a \gg 1$:

$$\mu_{\mathrm{el}} = \mu_{\mathrm{el}}^{\mathrm{Sm}}\left[1 - \frac{3}{2}\phi + O\left(\phi^{2}\right)\right]$$

Chen and Keh, AIChe **34** (1988); Ennis and White, J. Colloid Interface Sci. 185 (1997)

$$\frac{1}{V}\int_{V} d^3r\,\mathbf{u}(\mathbf{r};X) = \mathbf{0} \qquad \frac{1}{V}\int_{V} d^3r\left[\mathbf{E}(\mathbf{r};X) - \mathbf{E}_{\infty}\right] = \mathbf{0}$$

- Define particle velocity in bounded suspension relative to frame where the (particle plus fluid) velocity, averaged over whole suspension volume, is zero

Content

1. Introduction & Motivation
2. Low Reynolds number flow
3. Salient static properties
4. Electrophoresis of macroions
5. Dynamics of interacting Brownian particles
6. Short-time colloidal dynamics
7. Long - time colloidal dynamics
8. Primitive model electrokinetics

5. Dynamics of interacting Brownian particles

- Many-particle diffusion equation
- Dynamic simulations

5.1 Many - particles diffusion equation

- Probability conservation of configurational pdf:

$$\frac{\partial}{\partial t} P(X,t) + \sum_{i=1}^{N} \nabla_i \cdot \left(\mathbf{V}_i(X,t)\; P(X,t) \right) = 0$$

- Inertia-free motion (zero total force) for $t \gg \tau_B$

$$\mathbf{0} = \mathbf{F}_i^I + \mathbf{F}_i^e + \mathbf{F}_i^h + \mathbf{F}_i^B$$

Brownian force drives diffusion:

$$\mathbf{F}_i^B = -k_B T \nabla_i \ln P$$

Interaction forces:

$$\mathbf{F}_i^I = -\nabla_i V_N(\mathbf{r}^N)$$

Hydrodynamic drag forces (for $\mathbf{u}_\infty = 0$):

$$\mathbf{V}_i = -\sum_{l=1}^{N} \boldsymbol{\mu}_{il}^{tt}(X) \cdot \left(\mathbf{F}_l^h = -\mathbf{F}_l^I - \mathbf{F}_l^e - \mathbf{F}_l^B \right)$$

- N – particle generalized Smoluchowski equation (Kirkwood & Riseman)

$$\frac{\partial}{\partial t} P(X,t) = k_B T \sum_{i,j=1}^{N} \nabla_i \cdot \boldsymbol{\mu}_{ij}^{tt}(X) \cdot \left[\nabla_j - \beta \mathbf{F}_j^I - \beta \mathbf{F}_j^e \right] P(X,t)$$

Brownian motion $\propto$ T

$$P(X, t \to \infty) \to P_{eq}(X) \propto \exp\left[-\beta V_N(X) \right]$$

5.2 Dynamic simulations

- Discretized postional many – particle Langevin equation;

$$\mathbf{R}_i(t_0+\tau) = \mathbf{R}_i(t_0) + \sum_{j=1}^{N}\left[\boldsymbol{\mu}_{ij}^{tt}(X_0)\cdot\mathbf{F}_j(X_0) + k_B T\,\nabla_j\cdot\boldsymbol{\mu}_{ij}^{tt}(X_0)\right]\tau + \sqrt{2\tau}\sum_{j=1}^{N}\mathbf{d}_{ij}(X_0)\cdot\mathbf{n}_j + o(\tau)$$

DI & external

near-field HI
(hydrodyn. drift part)

central Gaussian
displacement

- Square - root mobility matrix **d** in random displacement:

$$k_B T\,\boldsymbol{\mu}^{tt}(X_0) = \mathbf{d}(X_0)\cdot\mathbf{d}^T(X_0)$$

$$\left\langle \Delta\mathbf{R}_i(\tau)\,\Delta\mathbf{R}_j(\tau)\right\rangle_0 = 2k_B T\,\boldsymbol{\mu}_{ij}^{tt}(X_0)\,\tau + o(\tau)$$ ← HI - coupling of displacements of i & j

- (accelerated) Stokesian dynamics simulation method for Brownian particles

How to calculate correlation functions

$$C_{f\,g}(t) = \langle f(t)\, g^*(0) \rangle_{eq} = \int\int dX\, dX_0\, P(X, t \mid X_0) \left(P_{in}(X_0) = P_{eq}(X_0) \right) f(X)\, g^*(X_0)$$

Conditional pdf : $X_0 \rightarrow X$ during time t
(from Smoluchowski eq.)

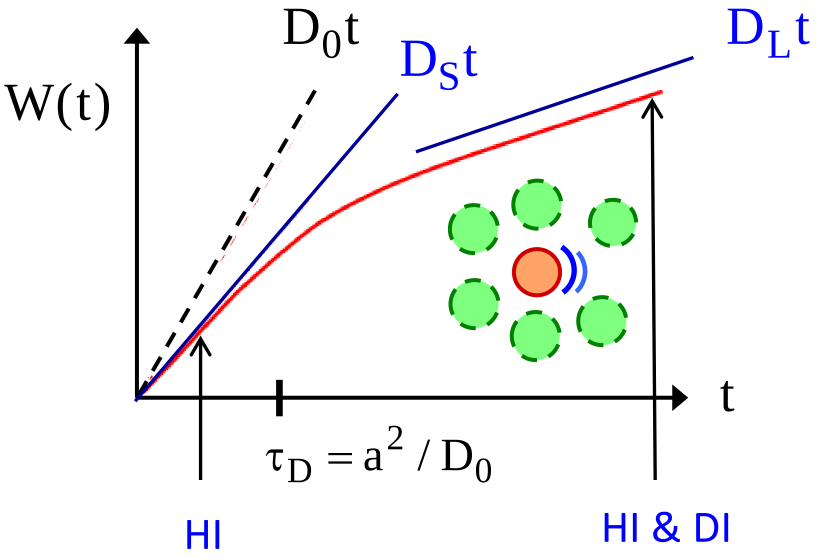
- Microscopic density fluctuations: $f(X) = g(X) = \int d^3r \exp(i\mathbf{q}\cdot\mathbf{r}) \sum_{l=1}^{N} \delta(\mathbf{r} - \mathbf{R}_l)$

- **Dynamic structure factor** measured in dynamic light scattering

$$S(q,t) = \lim_{\infty} \left\langle \frac{1}{N} \sum_{l,p=1}^{N} \exp\left\{ i\mathbf{q}\cdot\left[\mathbf{R}_l(t) - \mathbf{R}_p(0) \right] \right\} \right\rangle_{eq}$$

6. Short - time colloidal dynamics

- Hydrodynamic function
- Sedimentation
- High - frequency viscosity
- A simple BSA solution model
- Generalized SE relations

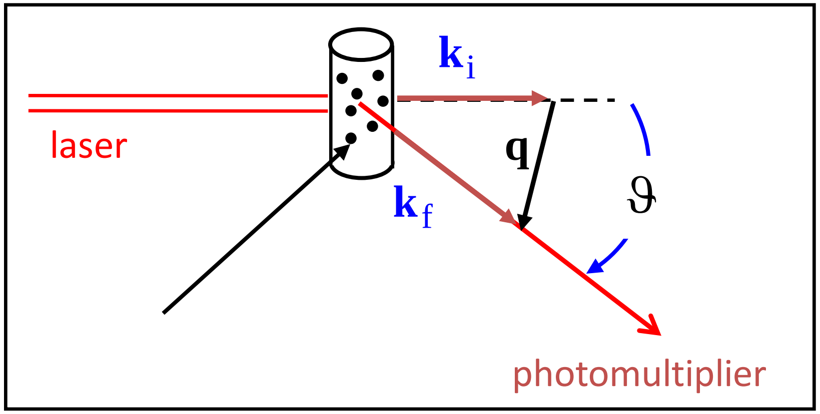


short - time resolution: $\tau_B \ll t \ll \tau_D$

6.1 Hydrodynamic function

- Dynamic structure factor S(q,t) is measured in dynamic scattering experiment:

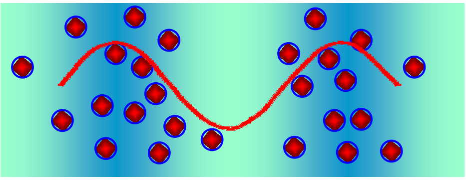
$$S(q,t \ll \tau_D) \approx S(q)\exp\left[-q^2 D(q)t\right]$$



$$D(q) = D_0 \frac{H(q)}{S(q)}$$

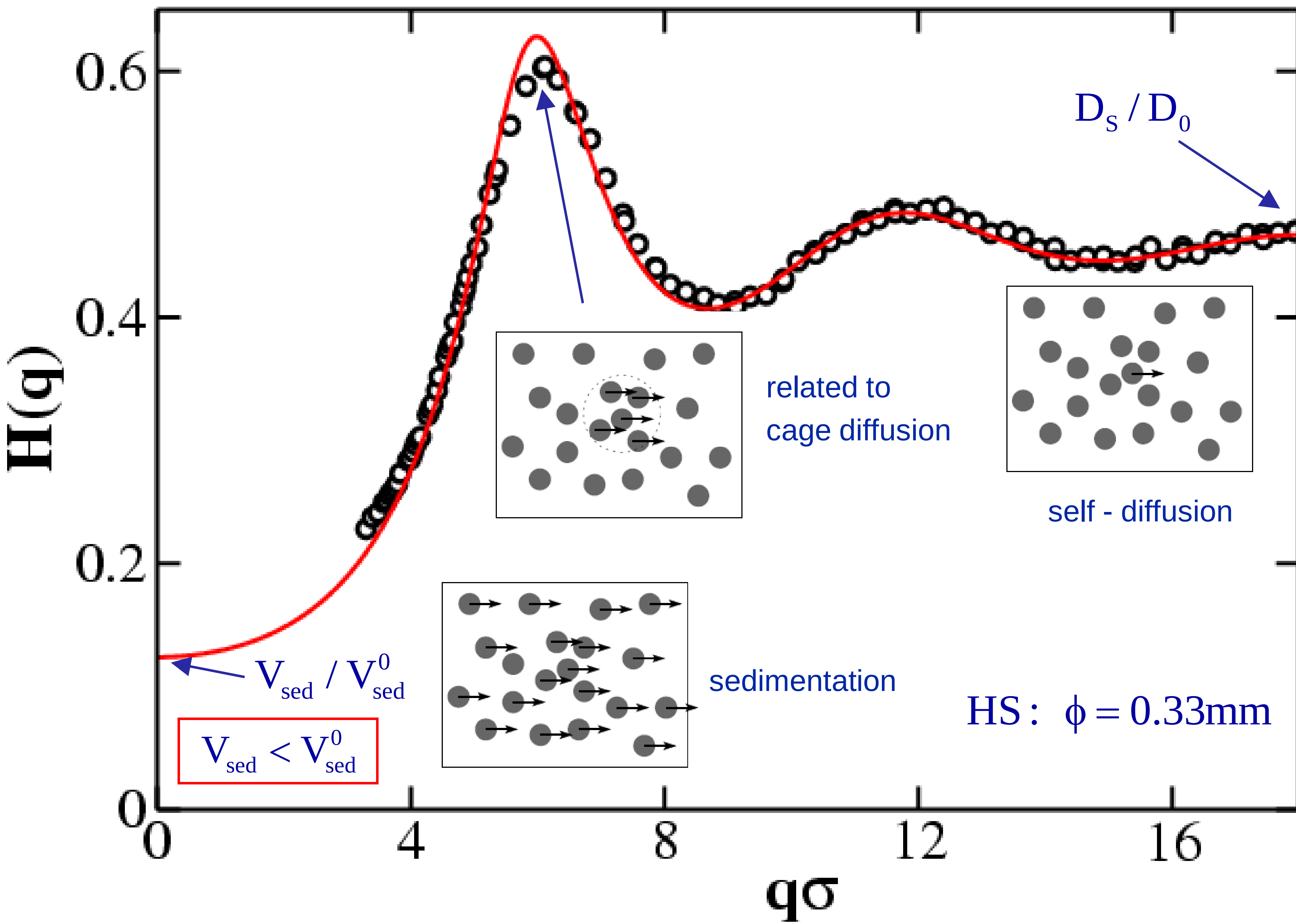
short - time diffusion function

$$H(q) = \lim_{\infty} \left\langle \frac{1}{N\mu_0^t} \sum_{p,\mathbf{j}=1}^{N} \hat{\mathbf{q}} \cdot \boldsymbol{\mu}_{p\mathbf{j}}^{tt}(X) \cdot \hat{\mathbf{q}} \exp[i\,\mathbf{q}\cdot(\mathbf{R}_p - \mathbf{R}_{\mathbf{j}})] \right\rangle_{eq}$$



$\longleftarrow 2\pi/q \longrightarrow$

H(q) = 1 without HI



H(q)
0.6
0.4
0.2
0
0
4
8
12
16
qσ
D_S / D_0
related to
cage diffusion
self - diffusion
sedimentation
V_{sed} / V^0_{sed}
$V_{sed} < V^0_{sed}$
HS : $\phi = 0.33$mm

Physical meaning: generalized sedimentation coefficient

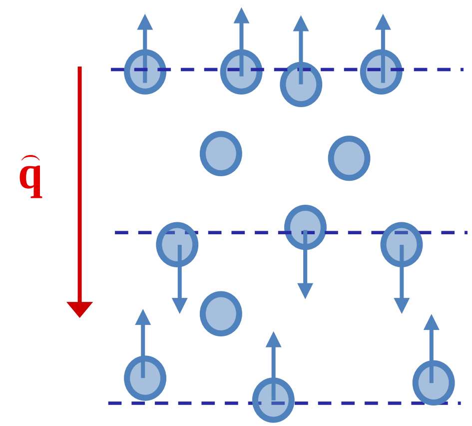
- Homogeneous system with spatially periodic force acting on each sphere **(linear response)**:

$$\mathbf{F}_j = \hat{\mathbf{q}} F^e \exp\left[i \mathbf{q} \cdot \mathbf{R}_j \right]$$ weak external force on sphere j

$$\langle V(q) \rangle_{st} = \lim_{\infty} \left\langle \frac{1}{N} \sum_{j=1}^{N} \hat{\mathbf{q}} \cdot \mathbf{V}_j \exp\left[i \mathbf{q} \cdot \mathbf{R}_j \right] \right\rangle_{st}$$ mean (short - time) response

$$\boxed{\langle V(q) \rangle_{st} = H(q)\, \mu_0\, F^e}$$

$$V^0_{sed} = \mu_0 F^e$$



$$\boxed{V_{sed} = \lim_{q \to 0} \left[\langle V(q) \rangle_{st} - \hat{\mathbf{q}} \cdot \lim_{\infty} \frac{1}{V} \int d^3 r \exp\{ i \mathbf{q} \cdot \mathbf{r} \} \mathbf{u}_{susp}(\mathbf{r}; X) \right]}$$

- **suspension velocity field**

$$\boxed{\nabla \cdot \mathbf{u}_{susp} = 0 \;\Rightarrow\; \mathbf{q} \cdot \mathbf{u}_{susp}(\mathbf{q}; X) = 0}$$

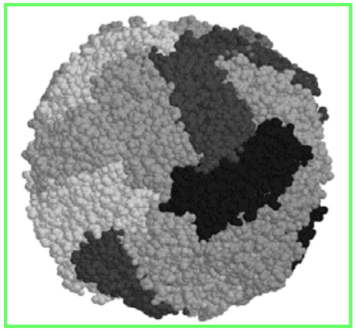
- **Lab frame** = zero volume flux frame
- (Short-time) sedimentation velocity in zero - volume flux reference system

Employed methods of Calculation

- **Accelerated Stokesian Dynamics (ASD) simulations** (Banchio & Brady, J. Chem. Phys., 2003)
  - extended to Yukawa – type charged colloids
  - lubrication effects disregarded
- **$\delta\gamma$ method** (Beenakker & Mazur, 1984) **with self - part correction**
  - truncated expansion in renormalized density fluctuations $\delta\gamma$
  - approximate inclusion of many-body HI only
  - lubrication effects disregarded
- **Pairwise - additive HI approximation for charged particles**
  - full inclusion of 2-body HI (tables by Jeffrey)
  - positive definiteness of mobility matrix not guaranteed
  - „exact“ to first order in concentration only
- **Rotne - Prager far- field hydrodynamic mobility tensors**
  - positive definiteness of hydrodynamic mobility matrix guaranteed
  - well-suited for charge-stabilized colloids at lower salinity

only input: S(q)

H(q) for Apoferritin protein solution (Yukawa - particle model)



symbols: ASD simulation

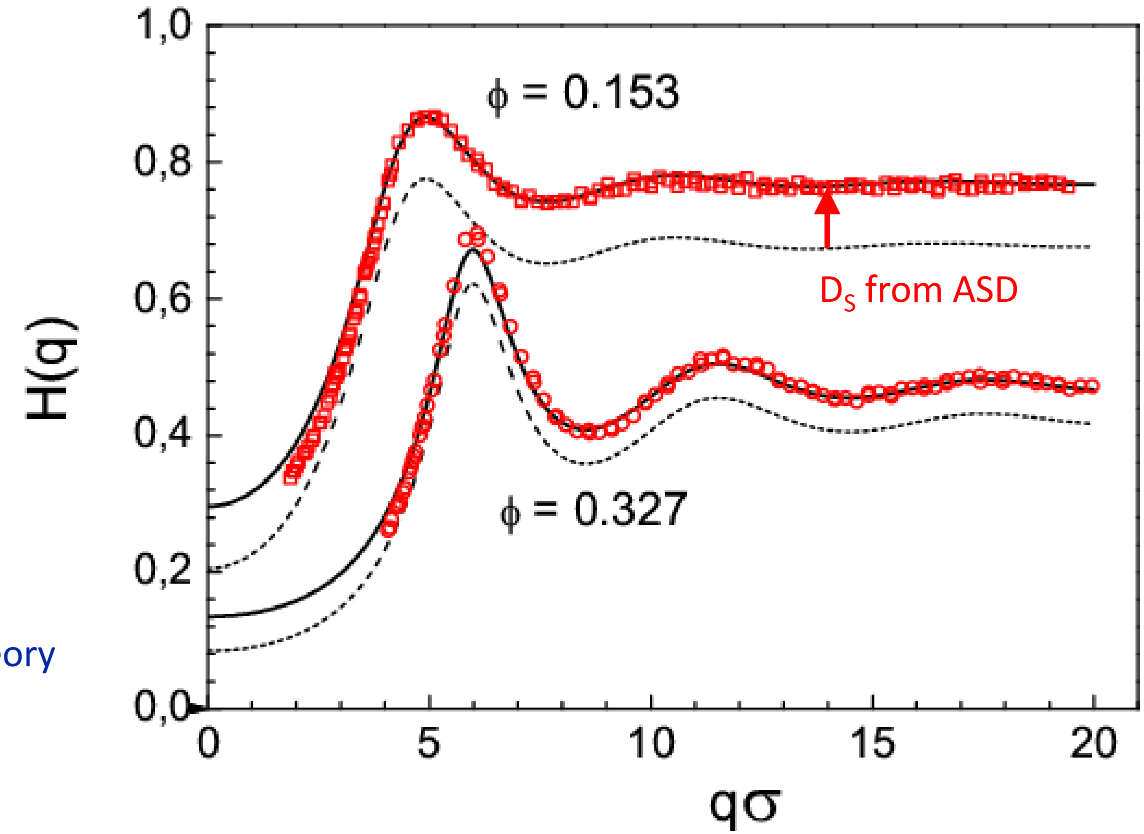
dashed : $\delta\gamma$ - theory

solid: self-part corr. $\delta\gamma$ -theory

$$H(q) = D_s / D_0 + H_d(q)$$

Input in self-part corrected $\delta\gamma$ - theory: ASD for $\phi > 0.1$

PA - theory for $\phi < 0.1$



Nägele, Banchio, Pecora, Patkowski et al
JCP **123** (2005)

- self-part corrected Beenakker – Mazur theory works well for distinct part of H(q)

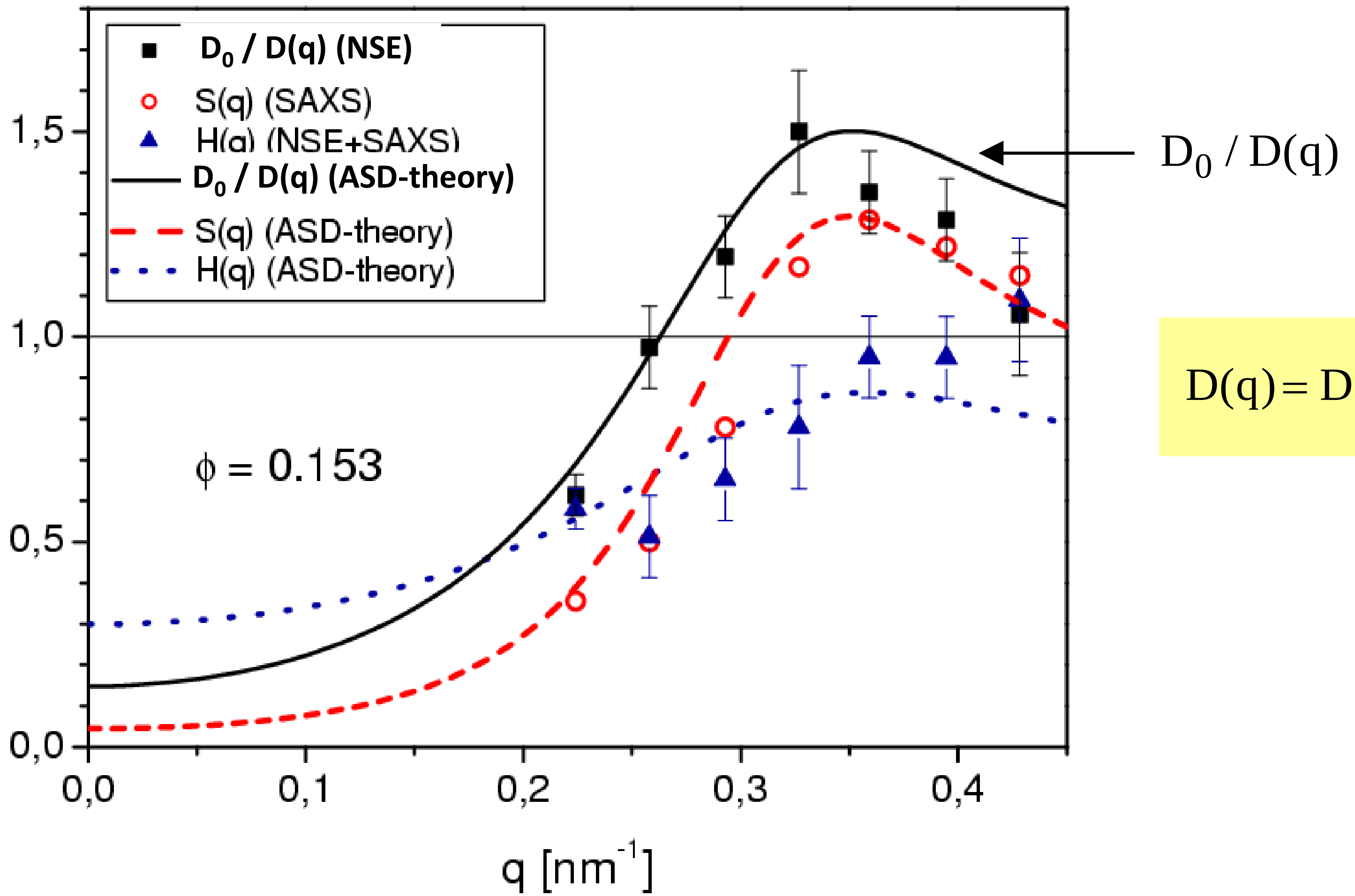
- self-part corrected Beenakker – Mazur theory works well for distinct part of H(q)

  (empirical finding for **all** ASD-simulated hard-sphere + Yukawa systems!)

- Critical assessment and improvements over the Beenakker - Mazur theory:

  Karol Makuch and B. Cichocki, J. Chem. Phys. **137** (2012) → **Poster 18**

Apoferritin : NSE experiment versus theory and simulation

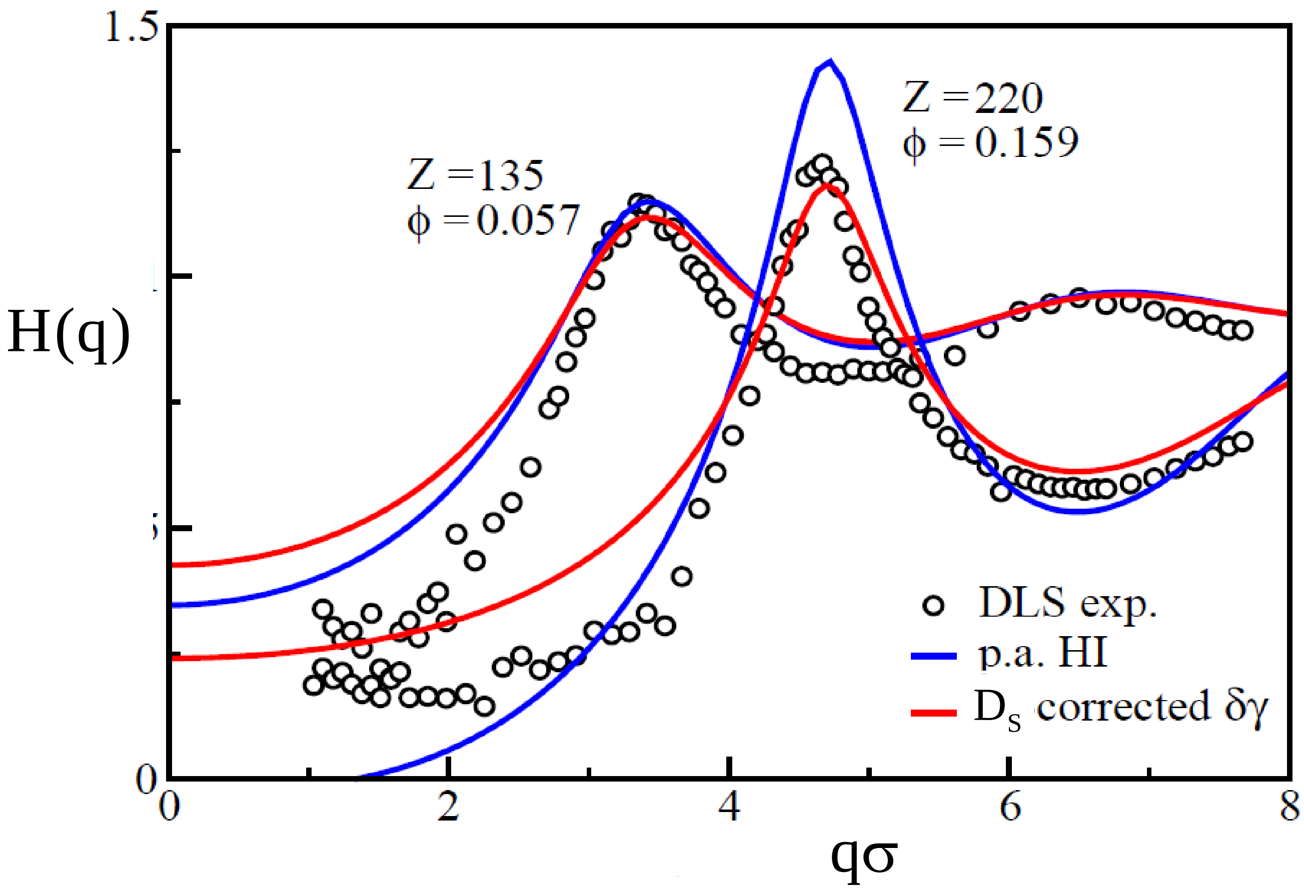


$$D(q) = D_0 \frac{H(q)}{S(q)}$$

- Reasonably good agreement between experiment and theory / simulation

Nägele, Banchio, Pecora, Patkowski et al
JCP **123** (2005)

Large charged colloidal spheres: Experiment and theory

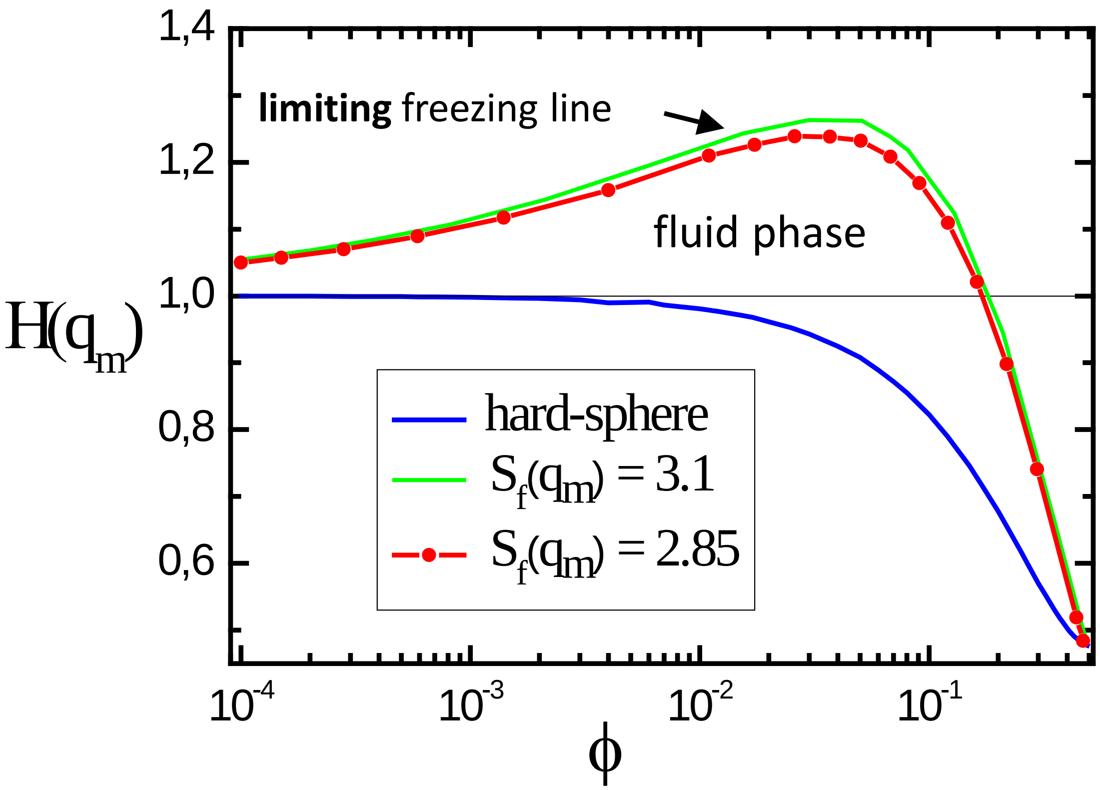


- Pairwise additive HI: good for low ϕ only, disregards HI shielding (μ^{tt} not positive definite)
- Self-part corrected $\delta\gamma$ - theory: close to exp. & simulation throughout liquid phase

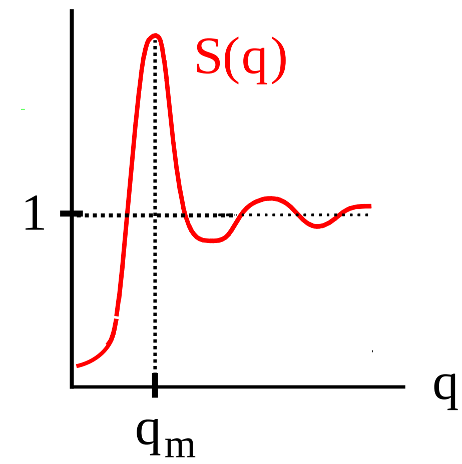
M. Heinen, P. Holmqvist, A. Banchio & G. Nägele, J. Appl. Cryst. **43** (2010) & J. Chem. Phys. **135** (2011)

Microgels: Holmqvist, Mohanty, Nägele, Schurtenberger, Heinen: Phys. Rev. Lett. **109** (2012)

Hydrodynamic function peak height at freezing (Yukawa + HS potential)



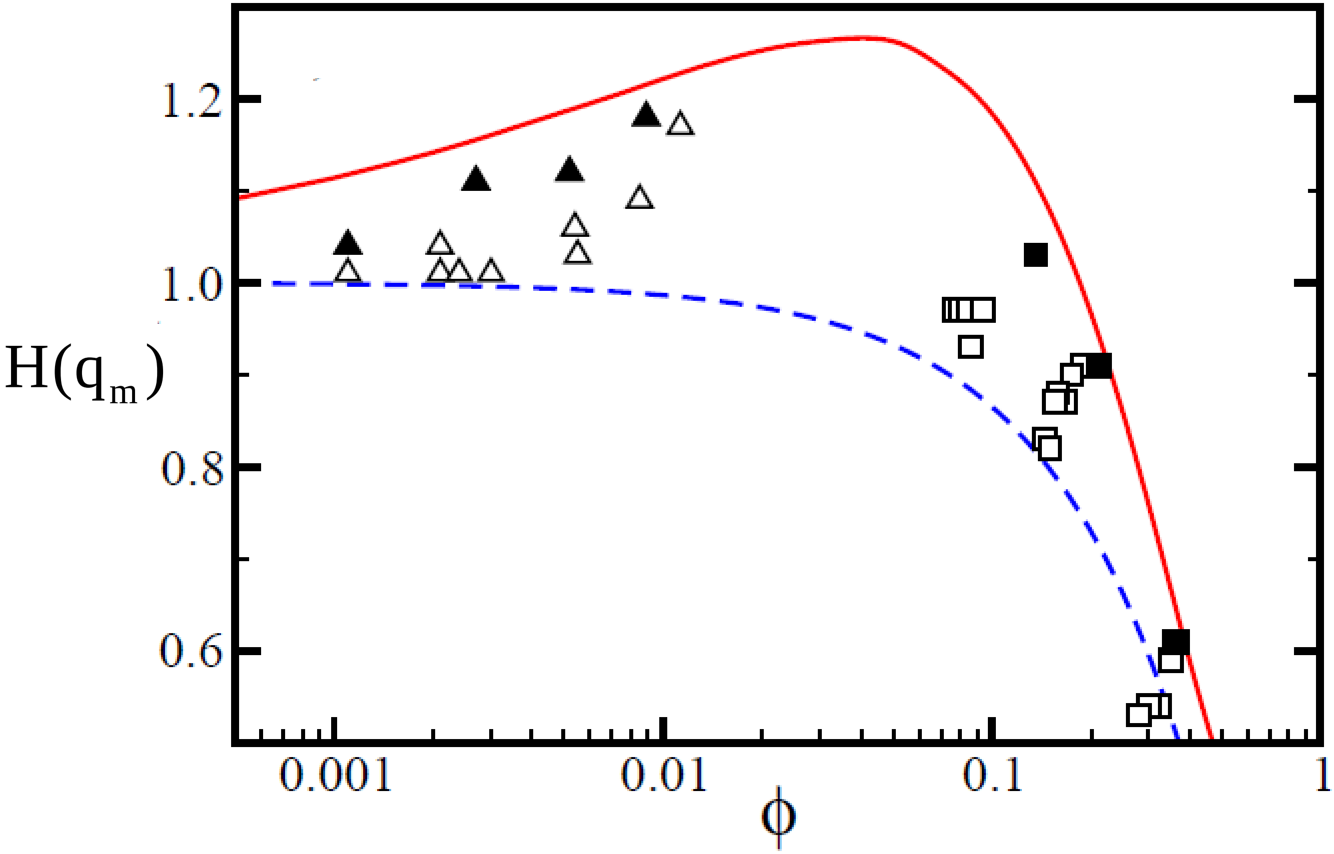
$$H_{HS}(q_m) = 1 - 1.35\phi$$



- **Universal** fluid - phase area is **insensitive** to Hansen - Verlet criterion value
- Provides map of attainable peak values of H(q) in fluid phase state

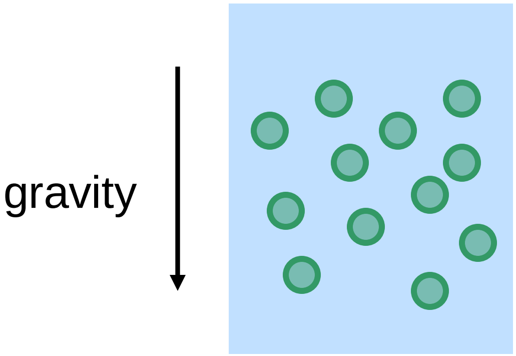
Gapinski, Patkowski & Nägele, J. Chem. Phys. **132**, 054510 (2010)

Comprehensive XPCS study of charge-stabilized poly-acrylate sphere suspensions



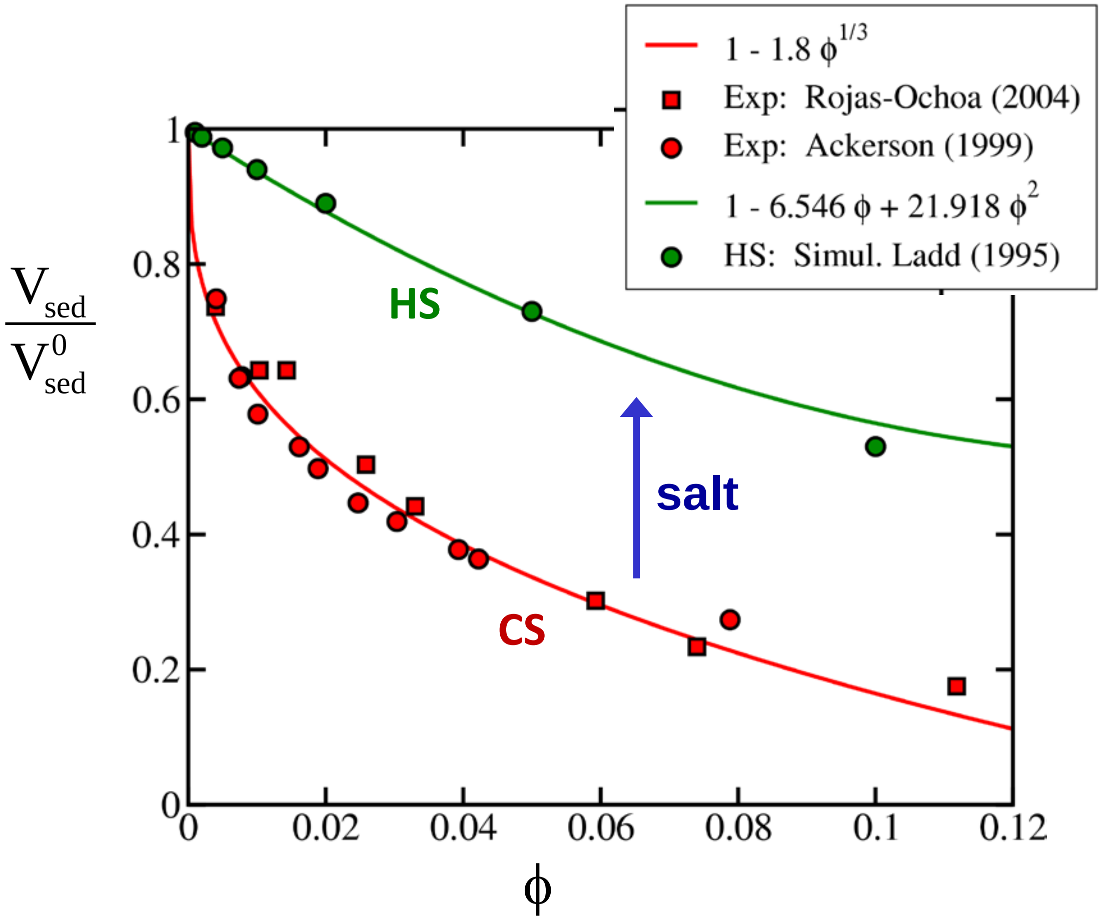
Westermeier, Heinen, Nägele et al.. J. Chem. Phys. **137** (2012)

6.2 Sedimentation



$$V_{sed} / V_{sed}^0 \approx 1 - 1.8\phi^{1/3}$$

- this is not a crystal !

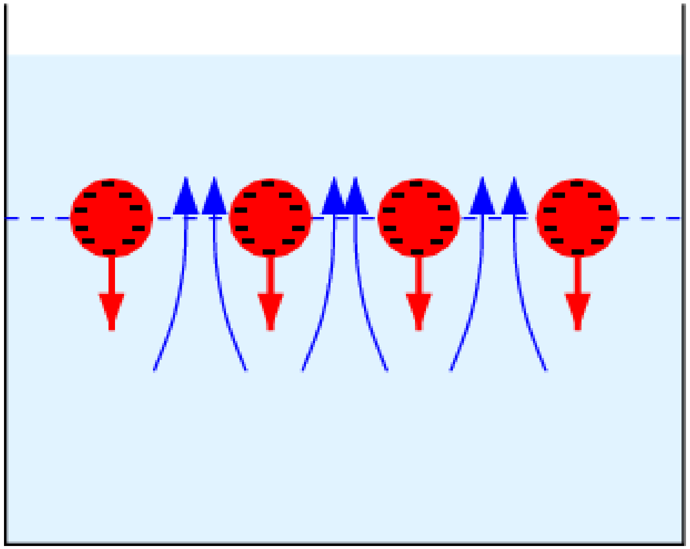


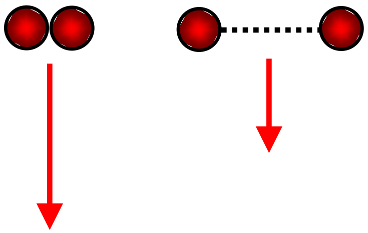
➢ Slower sedimentation of charged clay particles **(river - delta)**

ASD:: Banchio & Nägele, JCP **127**, 2008

Watzlawek & Nägele; JCIS **214** (1997)

Plausibility argument

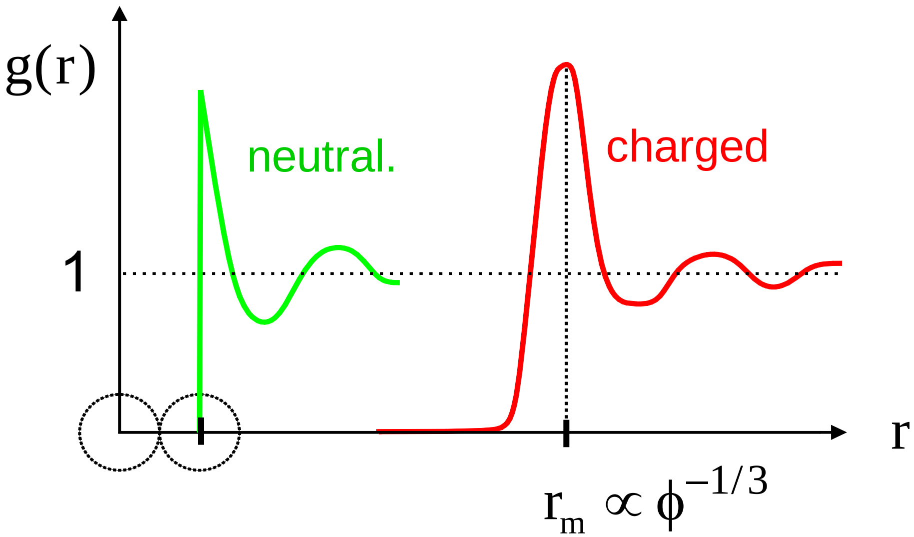




$$\nabla \langle p \rangle_{sa} = n \mathbf{F}^e$$

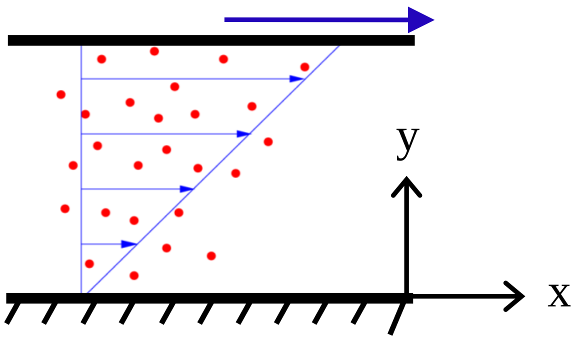
Pressure gradient drives

homogeneous mean fluid backflow



- Increased friction with backflowing fluid

6.3 High – frequency viscosity



$$\mathbf{u}_\infty = \dot{\gamma}\, y\, \hat{\mathbf{x}}$$

$$\langle \ldots \rangle_{st} = \int dX\, P_{st}(X;\dot{\gamma}) \ldots$$

- Macroscopic steady-state shear stress

$$\Sigma_{xy} = \langle \sigma_{xy}(\mathbf{r};X) \rangle_{st} = \frac{\mathbf{F}_x}{A} = \eta \frac{d(\mathbf{u}_\infty)_x}{dy} = \dot{\gamma}\,\eta$$

- Effective suspension viscosity

$$\eta(\dot{\gamma}) = \eta_\infty + \Delta\eta = \frac{1}{\dot{\gamma}}\Sigma^H_{xy} + \frac{1}{\dot{\gamma}}\left(\Sigma^I_{xy} + \Sigma^B_{xy}\right)$$

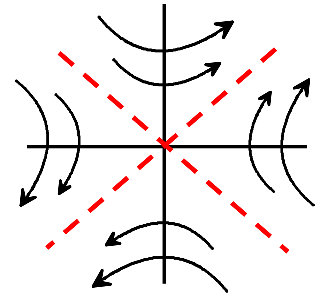
shear relaxation contribution ($\Delta\eta$) — DI (Σ^I_{xy}) — Brownian forces $\propto$ T (Σ^B_{xy})

- High - frequency viscosity part (HI only):

$$\eta_\infty(\dot{\gamma}) = \eta_0 + \frac{n}{\dot{\gamma}}\langle S^H_{xy}(X) \rangle_{st,ren}$$

symmetric force dipole (stresslet) (S^H_{xy})

$$\begin{pmatrix} V - e_\infty \cdot X \\ -S^H \end{pmatrix} = -\begin{pmatrix} \mu^{tt}(X) & \mu^{td}(X) \\ \mu^{dt}(X) & \mu^{dd}(X) \end{pmatrix} \cdot \begin{pmatrix} F^h = -(F^I + F^B) \\ -e_\infty \end{pmatrix}$$



- Strain-flow part: $\mathbf{e}_\infty \cdot \mathbf{r} = \dot{\gamma}\left[y\,\hat{\mathbf{x}} + x\,\hat{\mathbf{y}}\right]/2$

- Shear – relaxation viscosity part:

$$\Delta\eta(\dot\gamma) = -\frac{n}{\dot\gamma^2}\left\langle \mathbf{V}_i^c \cdot \left(\mathbf{F}_i^I + \mathbf{F}_i^B\right)\right\rangle_{st,ren} = \frac{1}{\dot\gamma}\left(\Sigma_{xy}^I + \Sigma_{xy}^B\right)$$

$$\mathbf{F}_i^I + \mathbf{F}_i^B = -\nabla_i V_N(X) - k_B T \, \nabla_i \ln P_{st}(X) \propto \dot\gamma$$

$$\mathbf{V}_i^c(X) = \left[\mathbf{1} \otimes \mathbf{R}_i + \boldsymbol{\mu}_i^{td}(X)\right] : \mathbf{e}_\infty \propto \dot\gamma$$

Convective velocity (particle force- and torque free)

HIs: 3rd rank shear mobility tensor of particle i

- Shear – Péclet number:

$$Pe = \frac{\text{diffusion time}}{\text{flow time}} = \frac{\tau_D}{\tau_{\dot\gamma}} = \frac{a^2 / D_0}{1/\dot\gamma} \propto \dot\gamma \, a^3$$

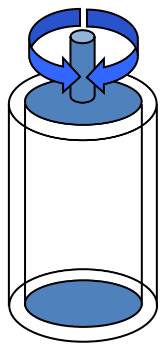
G.K. Batchelor, J. Fluid Mech. **83**, 97 (1977)

W.B. Russel, J. Chem. Soc. Faraday Trans. **2**, 80 (1984)

G. Nägele and J. Bergenholtz, J. Chem. Phys. **108** (1998) → **Green-Kubo relation and MCT for mixtures**

High-frequency viscosity of no - slip Brownian hard spheres

$$\omega \gg (\tau_D)^{-1}$$
$$Pe = \dot{\gamma}\,\tau_D << 1$$

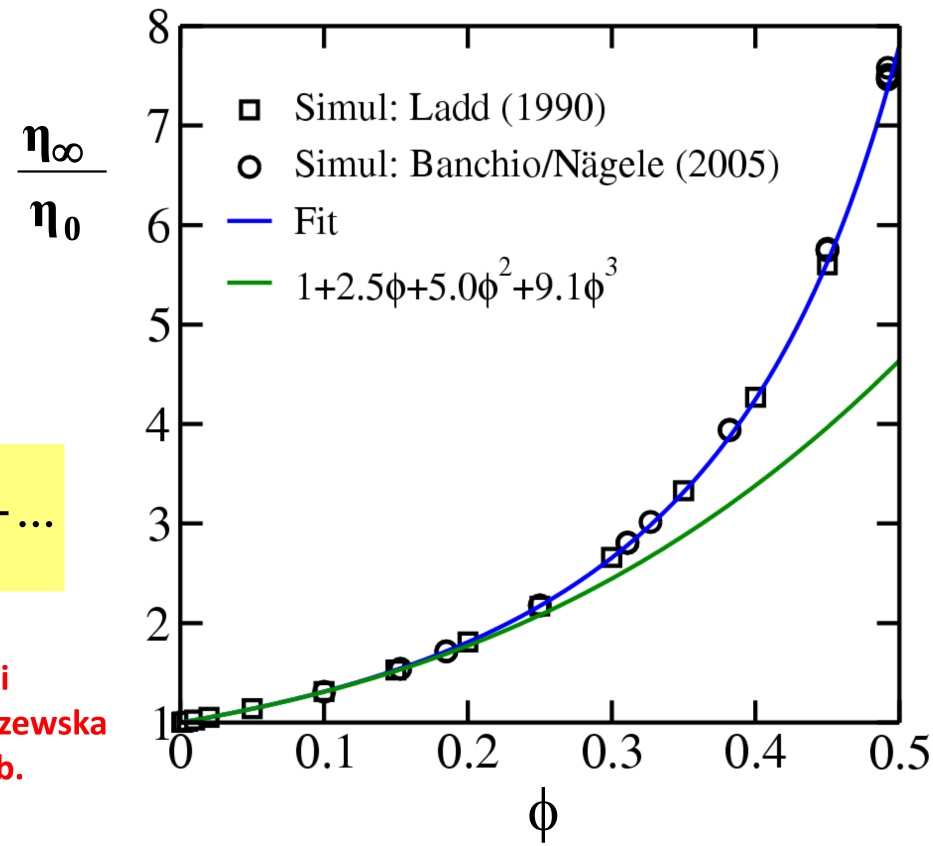


$$\frac{\eta_\infty(\dot{\gamma} \to 0)}{\eta_0} = 1 + 2.5\phi + 5.0\phi^2 + 9.1\phi^3 + \ldots$$

Einstein
1905: 1.0
1911: 2.5 (Hopf)

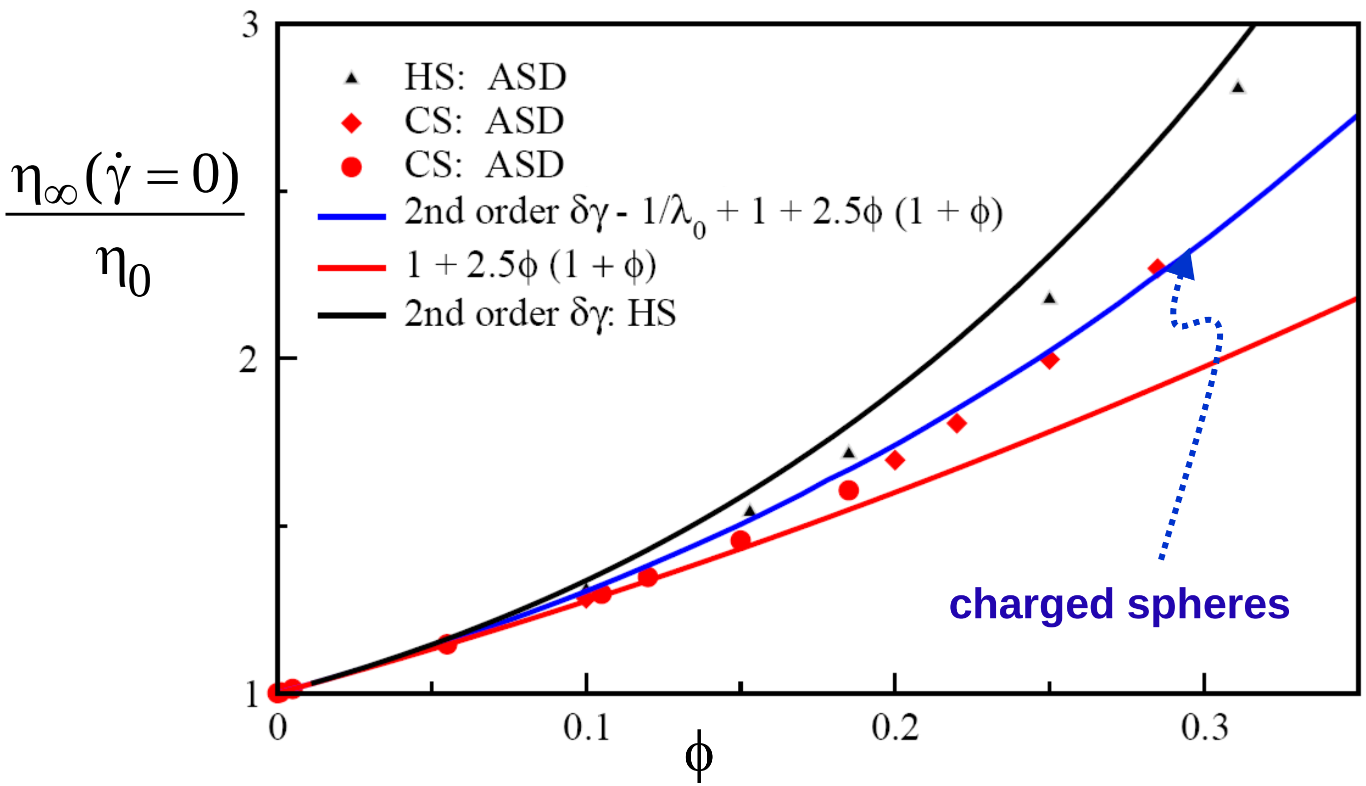
Batchelor & Green
(1972)

Cichocki
Ekiel-Jezewska
Wajnryb.
(2003)

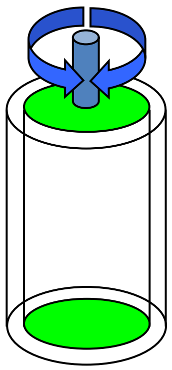


- Virial expansion in volume fraction applicable to lower concentrations only

High - frequency viscosity of charged Brownian spheres



$\omega \gg (\tau_D)^{-1}$



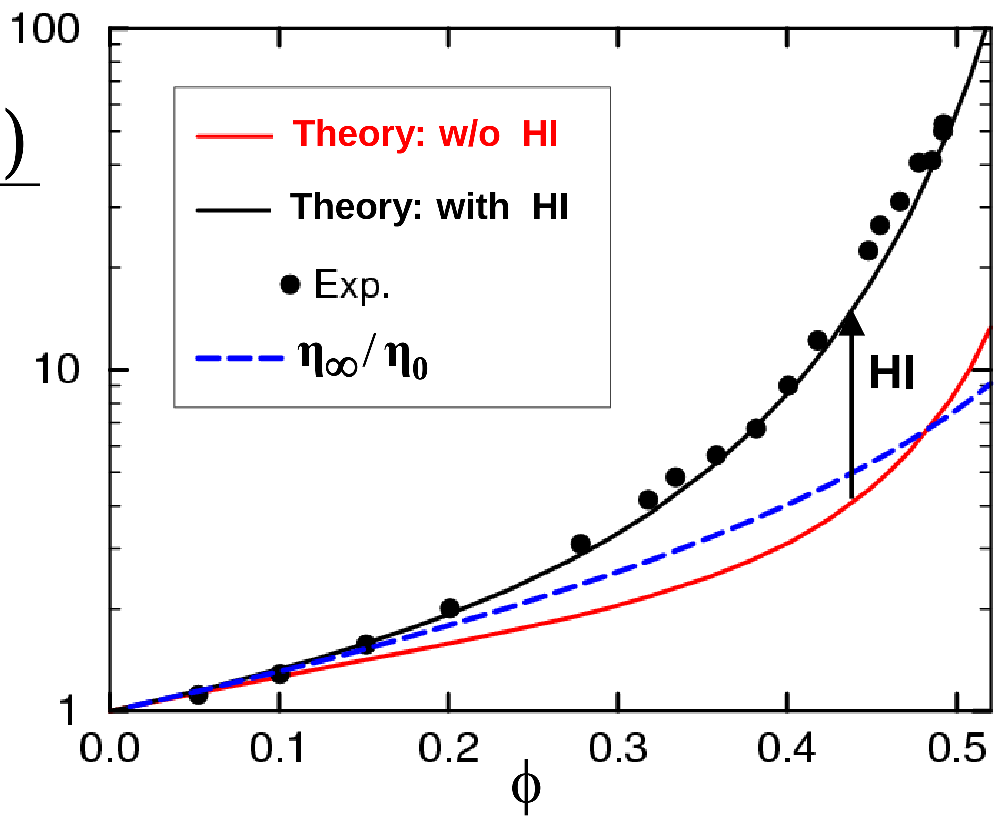
$\eta = \eta_\infty + \Delta\eta$

- Lower high – frequency viscosity for charged spheres (CS)
- But: $\Delta\eta(\mathrm{CS}) > \Delta\eta(\mathrm{HS})$

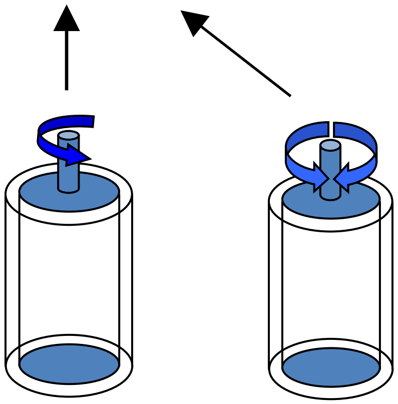
Heinen, Banchio & Nägele, J. Chem. Phys. **135** (2011)

Steady-state versus high-frequency viscosity of hard spheres

$$\frac{\eta(\dot{\gamma} \to 0)}{\eta_0}$$



$$\eta = \eta_\infty + \Delta\eta$$



$$\frac{\eta(\dot{\gamma} \to 0)}{\eta_0} = 1 + 2.5\phi + 5.9\phi^2 + \ldots$$

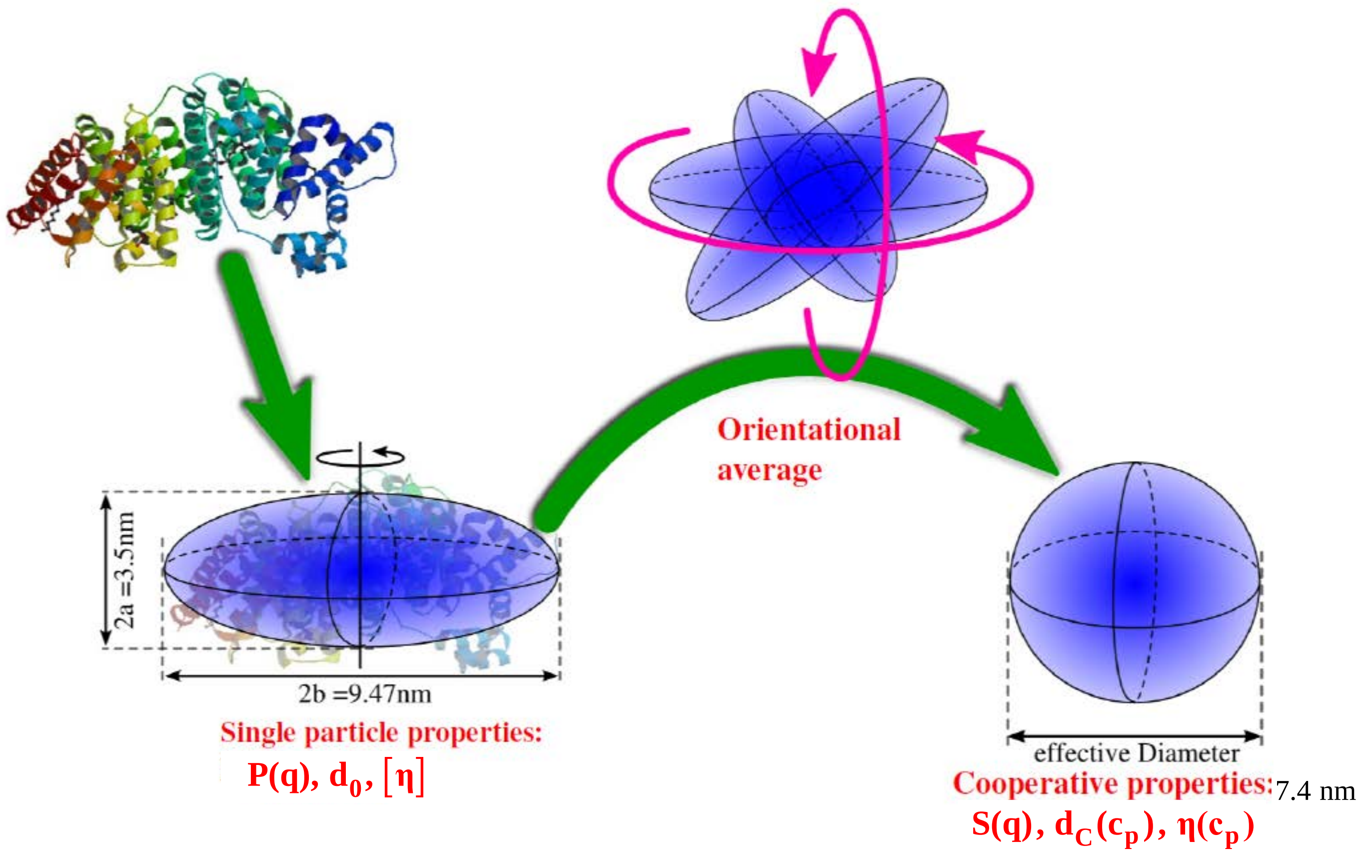
0.9 from Σ^{B}_{xy} $\left(\Sigma^{I}_{xy} = 0 \text{ for HS}\right)$

Batchelor (1972)

Theory: Banchio, Nägele, Bergenholtz, Phys. Rev. Lett..**82** (1999)

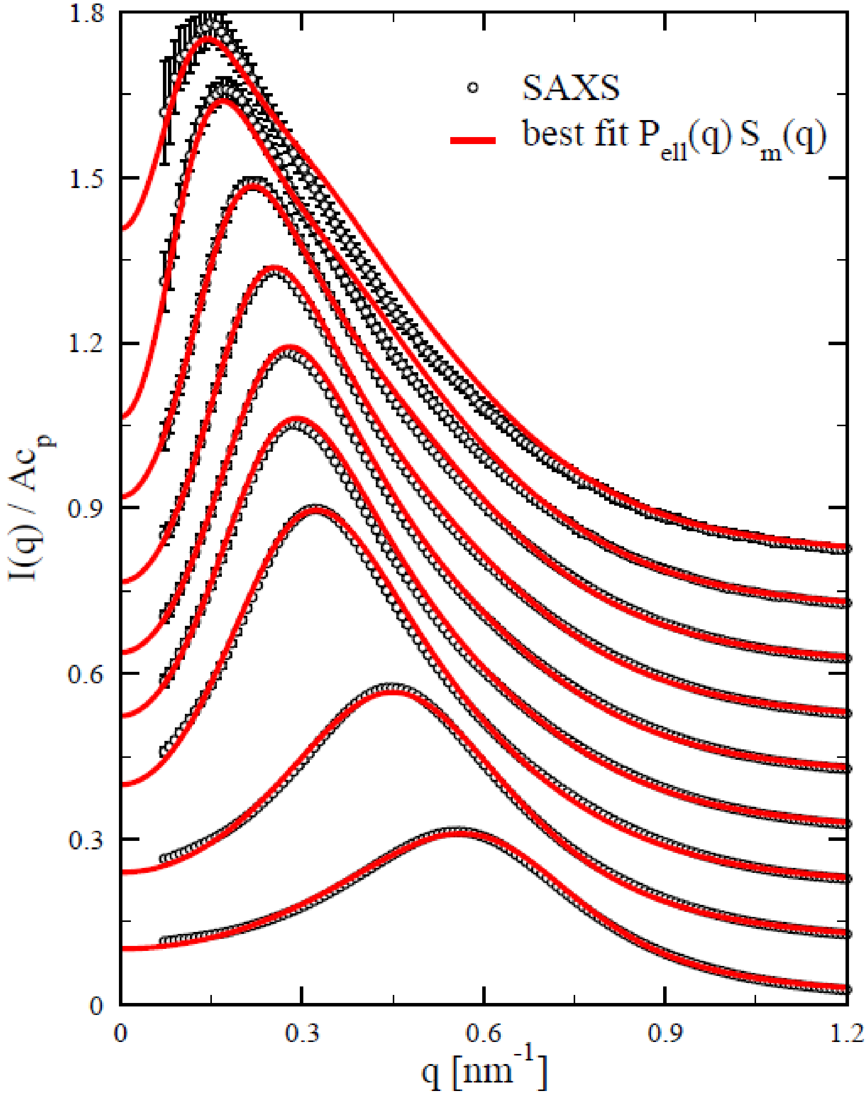
Exp.: Segrè et al., Phys. Rev. Lett. **75** (1995)

6.4 A simple BSA solution model



- Use screened Coulomb pair potential of DLVO type („Yukawa"-spheres) for direct interactions in combination with oblate spheroid form factor
- Empoy analytic methods for structure and (hydro-) dynamics of Yukawa spheres

Small angle X - ray scattering data fitting

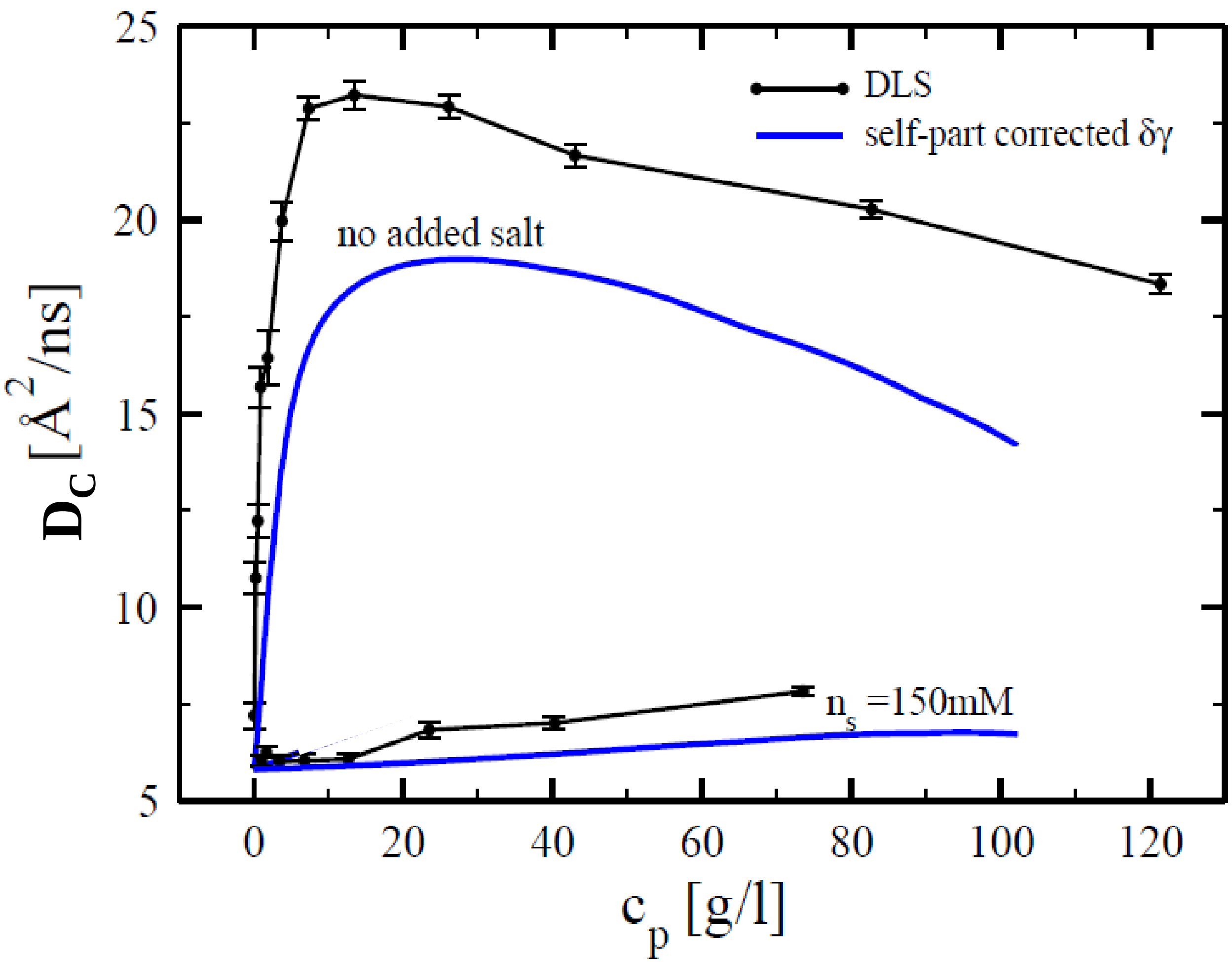


$c_p = 0.9\ mg/ml\ \ (\phi = 5.2 \times 10^{-4})$

$c_p = 90\ mg/ml\ \ (\phi = 0.17)$

Interaction parameters fully determined from SAXS fit

Collective (gradient) diffusion: DLS data versus theory

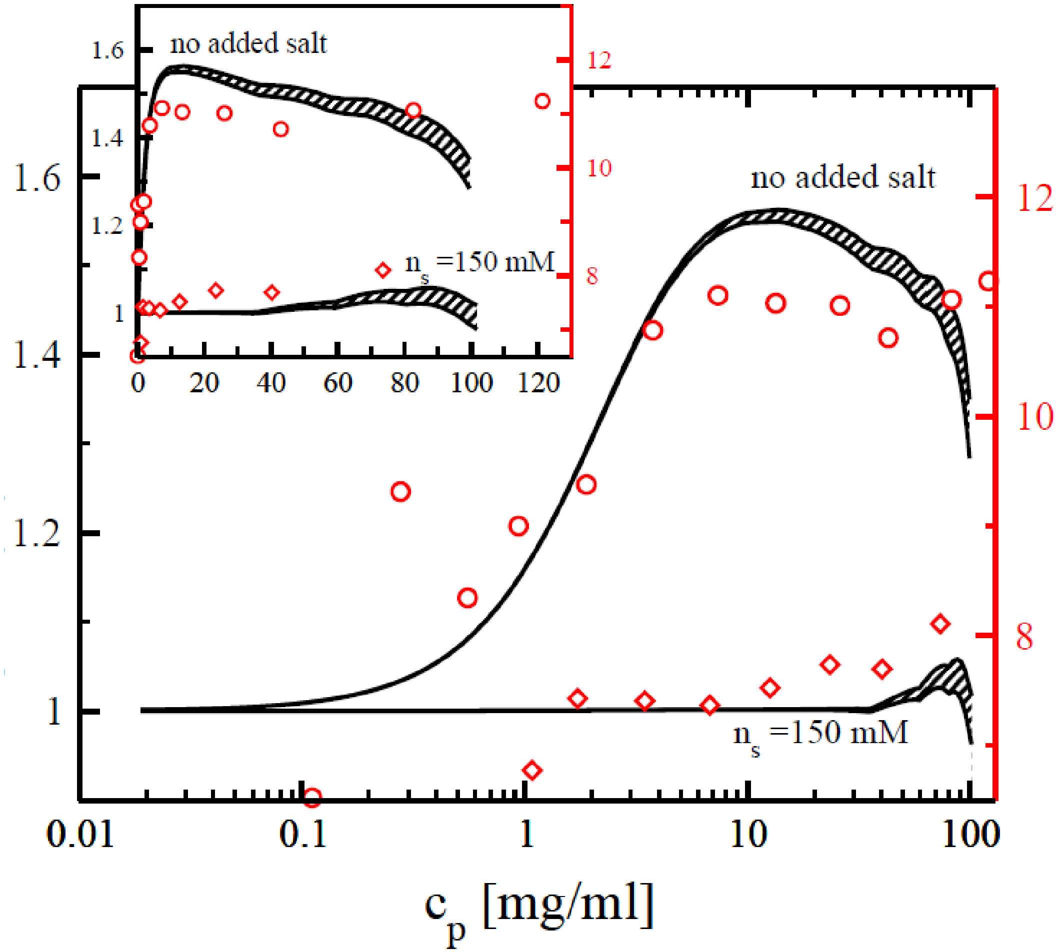


$$\frac{D_c}{D_0} = \frac{H(0)}{S(0)}$$

$$\mathbf{j}_C = -D_C \nabla c_p$$

- Difference explainable by: $D_0^{exp} / D_0^{theor} \approx 1.25$

Test of Kholodenko – Douglas GSE relation for BSA proteins



$$\frac{D_C}{D_0}\frac{\eta}{\eta_0}\sqrt{S(0)} \approx 1$$

Kholodenko & Douglas, PRE **51** (1994)

$$D_C \approx \frac{k_B T}{6\pi a \eta \sqrt{S(0)}}$$

KD – generalized Stokes-Einstein relation(s) violated at low salinity

M. Heinen, G. Nägele & F. Schreiber group (U of Tübingen): Soft Matter **8**, 2012 (2012)

6.5 Generalized short - time Stokes - Einstein (GSE) relations

Translational self-diffusion :

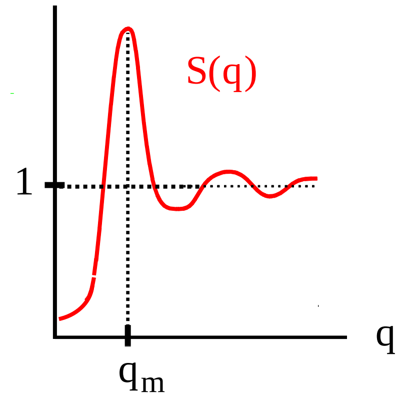
$$D_S(\phi) \overset{?}{\approx} \frac{k_B T}{6\pi\,\eta_\infty(\phi)\,a}$$

Rotational self-diffusion :

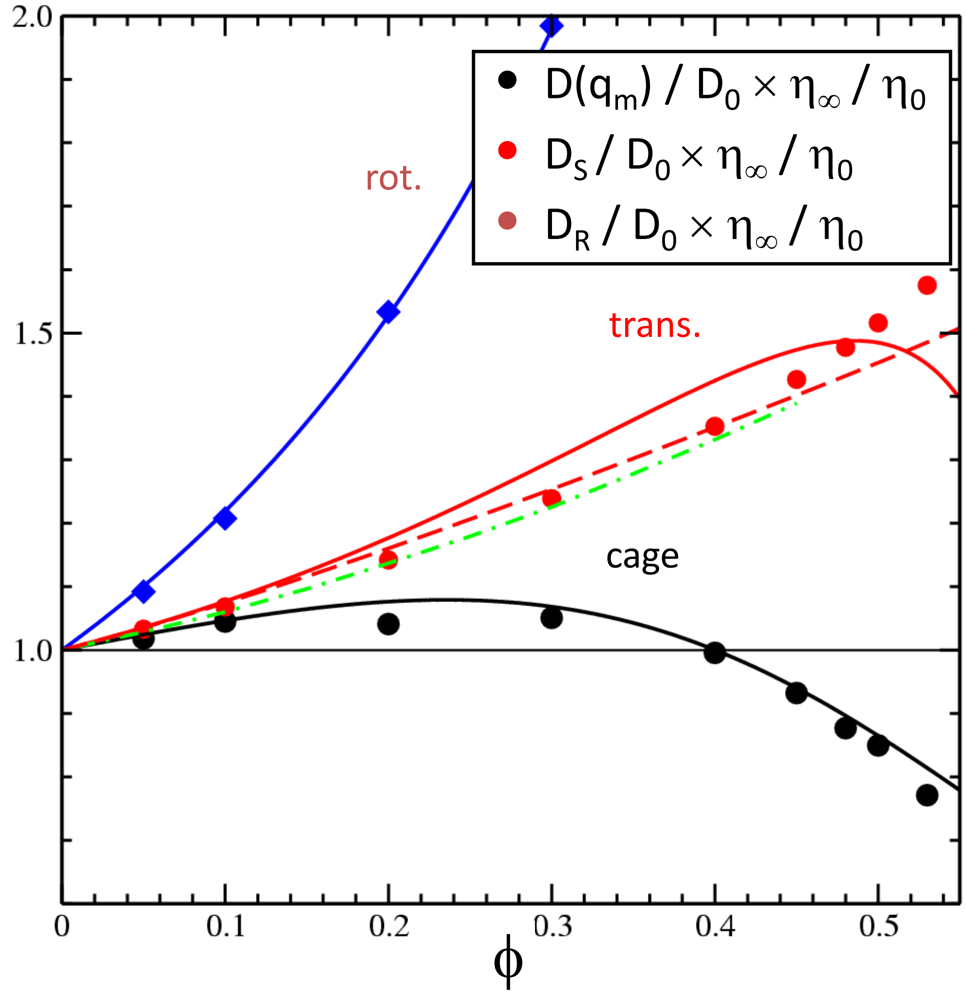
$$D_R(\phi) \overset{?}{\approx} \frac{k_B T}{8\pi\,\eta_\infty(\phi)\,a^3}$$

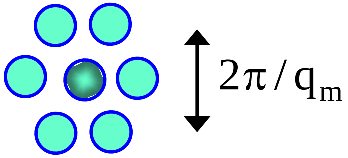
Cage diffusion coefficient:

$$D(q_m;\phi) = D_0 \frac{H(q_m)}{S(q_m)} \overset{?}{\approx} \frac{k_B T}{6\pi\,\eta_\infty(\phi)\,a}$$



Test of GSE relations for neutral colloidal hard spheres



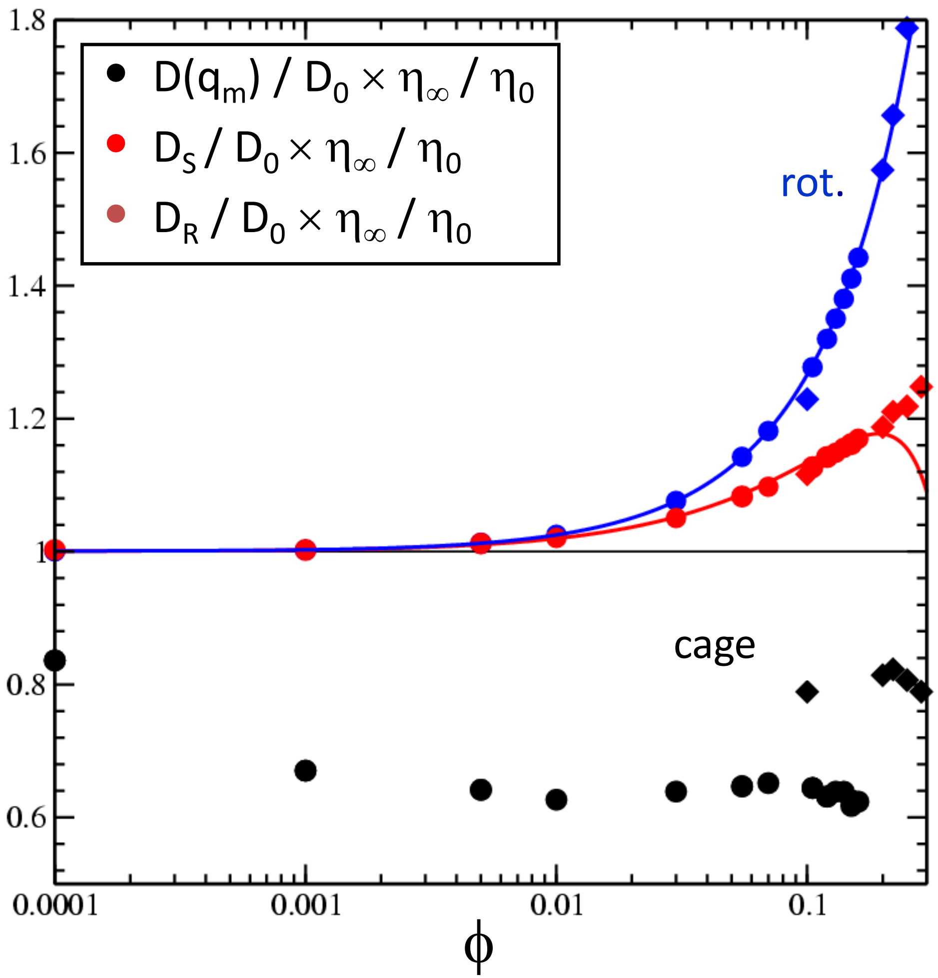


$$\frac{D(q_m)}{D_0} \approx \frac{\eta_0}{\eta_\infty}$$

Approximate validity of GSE relation depends crucialy on pair potential

Watch out when using GSE relations!

Test of GSE relations for charged spheres (HS +Yukawa)



Symbols: ASD simulations
Lines: analytic theory

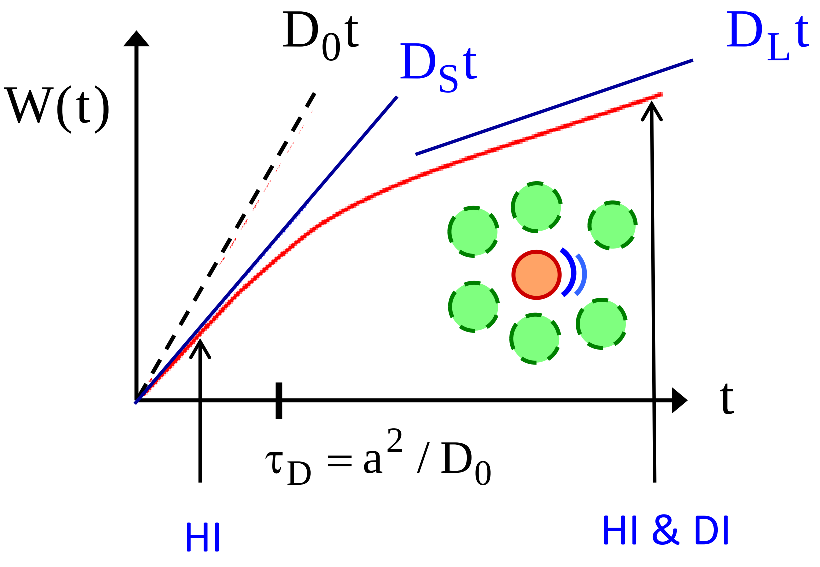
Banchio & Nägele
J. Chem. Phys. **128** (2008)

CS: Translational self - diffusion GSE satisfied fairly well, cage diffusion relation violated

HS: Cage diffusion GSE relation satisfied fairly well:

7. Long - time colloidal dynamics

- Memory equations and MCT
- HI enhancement of self-diffusion
- Self-diffusion of DNA fragments



7.1 Memory equation and mode coupling theory

$$\frac{\partial}{\partial t} S(q,t) = - q^2 D_0 \frac{H(q)}{S(q)} S(q,t) - \int_0^t du\, M_c^{irr}(q,t-u) \frac{\partial S(q,u)}{\partial u}$$

Memory function: includes non-instantaneous response of surrounding dynamic particle cage (relaxation effects)

→ Frequently applied approximation: mode couplingt theory

→ leads to self-consistent non-linear integro-differential eq. for S(q,t)

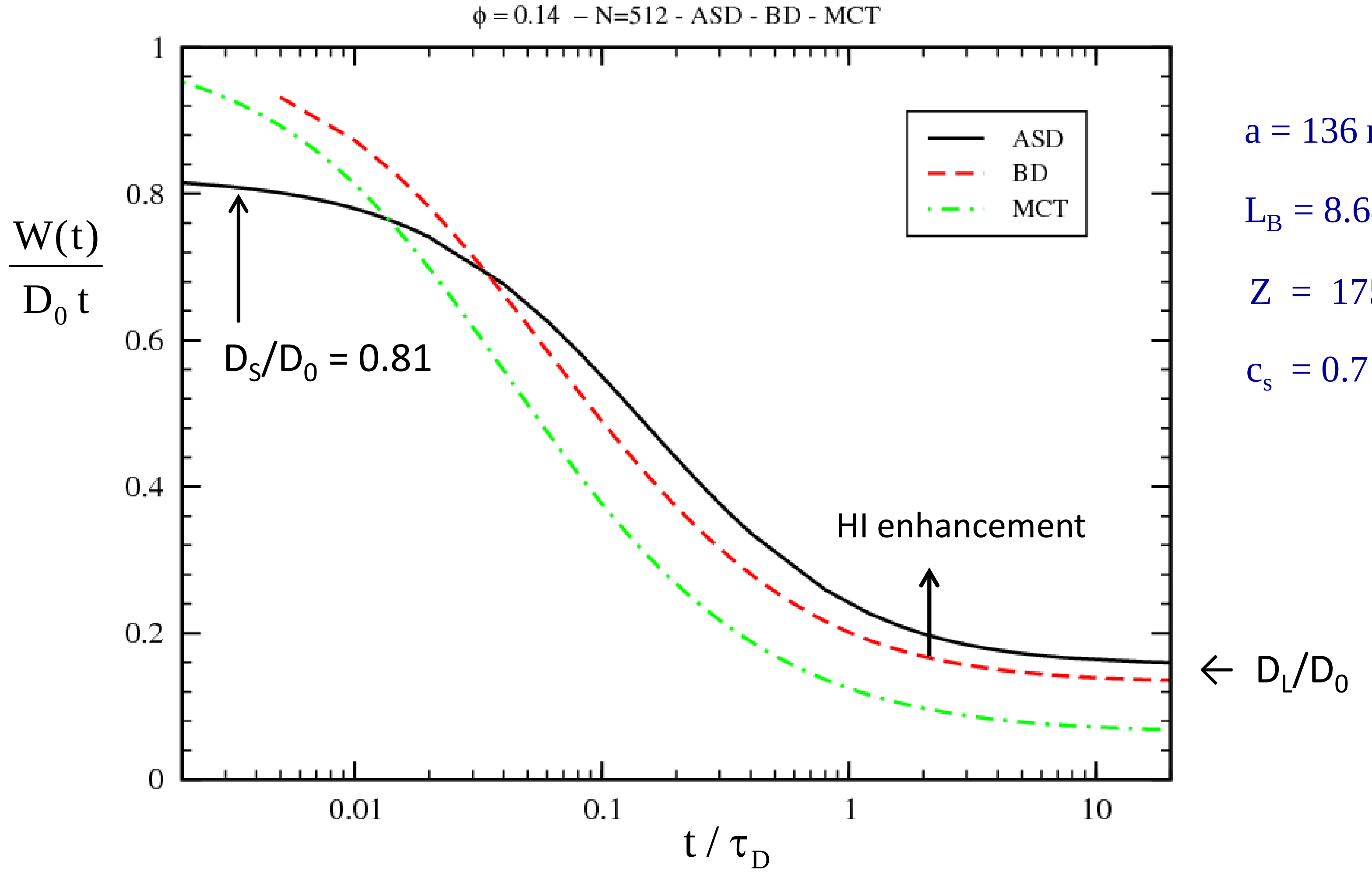
→ only input required is : S(q)

→ **Extension to Brownian mixtures and HI on Rotne Prager level:**:

G. Nägele er al., J. Chem. Phys. **108**, 9566 & 9893 (1998)

J. Chem. Phys. **110**, 7037 (1999)

7.2 HI enhancement of self - diffusion at low salinity



a = 136 nm

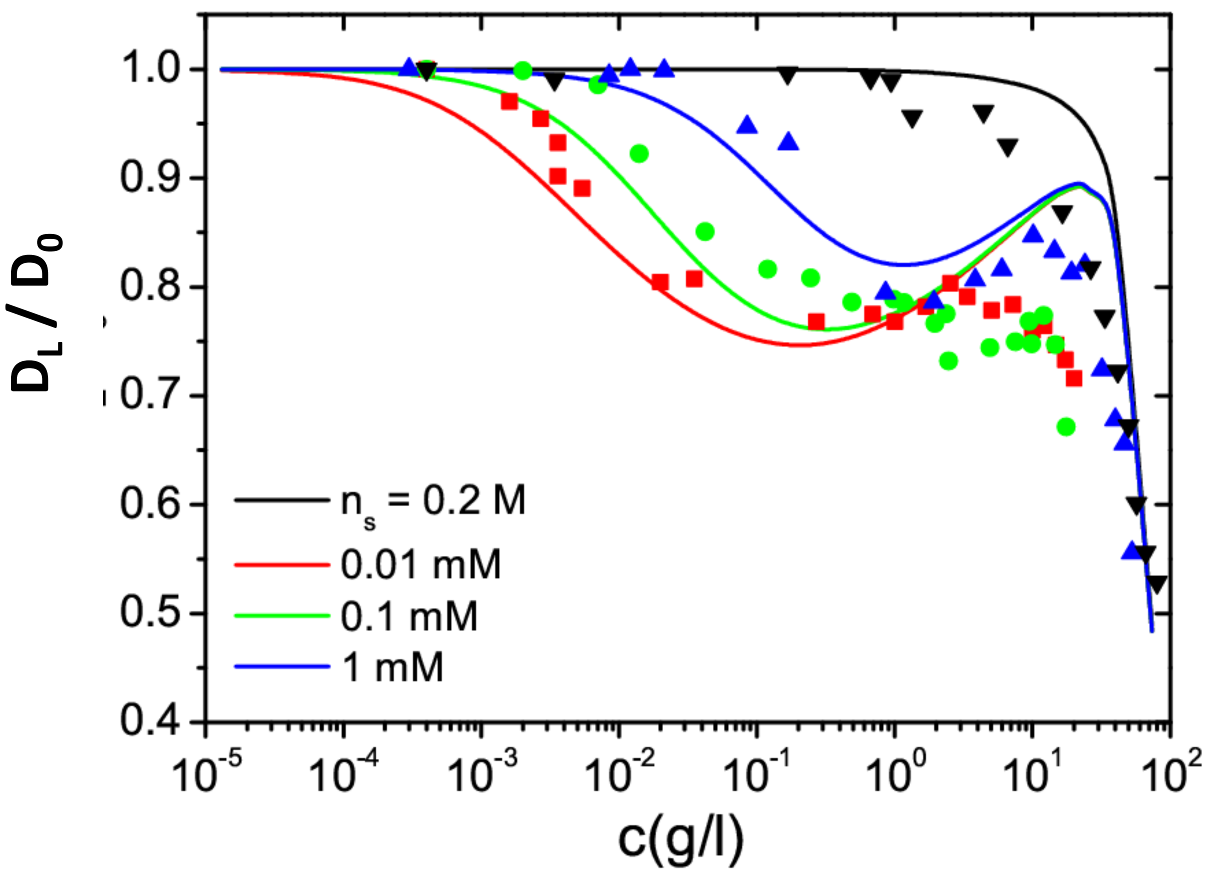
L_B = 8.64 nm

Z = 175 e

c_s = 0.7 μmol/l

A. Banchio, M. Heinen and G. Nägele, work to be submitted (2013)

7.3 Self-diffusion of DNA fragments



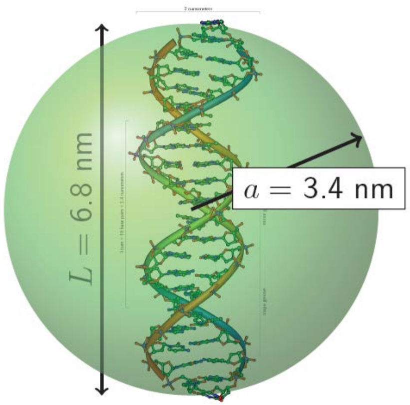
FCS experiments by:

Wilk, Patkowski, Pecora et al.

J. Chem. Phys. **121** (2004)

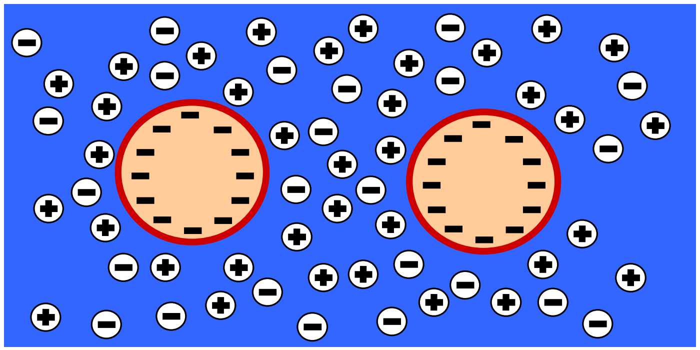
L = 6.8 nm

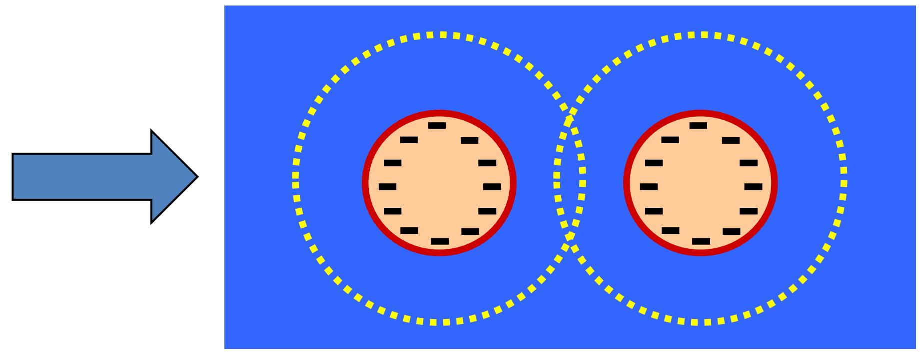
d = 2.0 nm



- Non – monotonous concentration dependence of short DNA fragments at low salinity
- **Physical origin ?**

Concentration dependence of effective colloid charge





$$\beta u_{ij}(r) = L_B \frac{Z_i Z_j}{r}$$

$$\beta u(r) = L_B Z_{eff}^2 \left(\frac{\exp[\kappa_{eff}\, a]}{1 + \kappa_{eff}\, a} \right)^2 \frac{\exp[-\kappa_{eff}\, r]}{r}$$

- Account of macroion charge - renormalization in jellium model : $Z_{bare} \rightarrow Z_{eff}$

(**due to counterion quasi - condensation**)

Renormalized jellium model (counterion quasi - condensation)

$$\Delta\phi(r>a) = -4\pi L_B\left[2c_s \sinh(\phi(r)) + n_{coll} Z_{back}\left(e^{\phi(r)} - 1\right)\right]$$

salt ions (1:1) — counterions — colloid jellium

$$\phi'(a) = -L_B Z/a^2$$

$$\phi'(\infty) = 0$$

$$Z_{eff}(Z_{back}; Z, n_{coll}, c_s) = Z_{back}$$

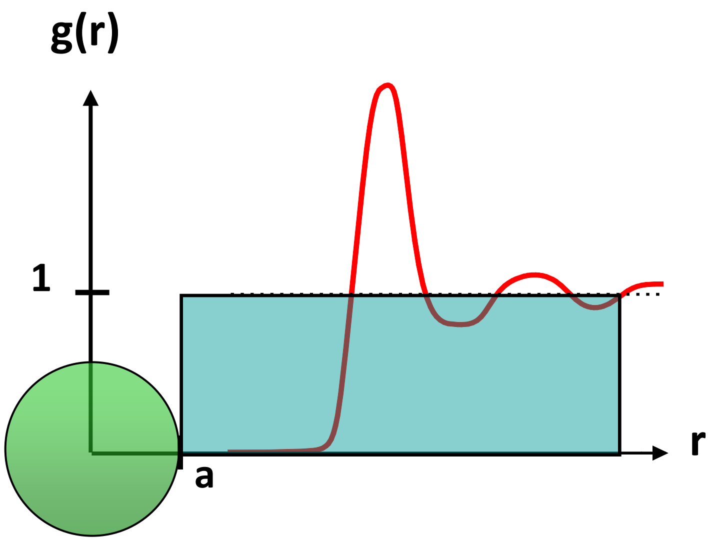
$$\phi(r \gg a) \approx L_B Z_{eff}^2 \left(\frac{e^{\kappa_{eff} a}}{1+\kappa_{eff} a}\right)^2 \frac{e^{-\kappa_{eff} r}}{r}$$

$$\kappa_{eff}^2 = 4\pi L_B [n_c Z_{eff} + 2n_s]$$

$$Z \rightarrow Z_{eff}$$

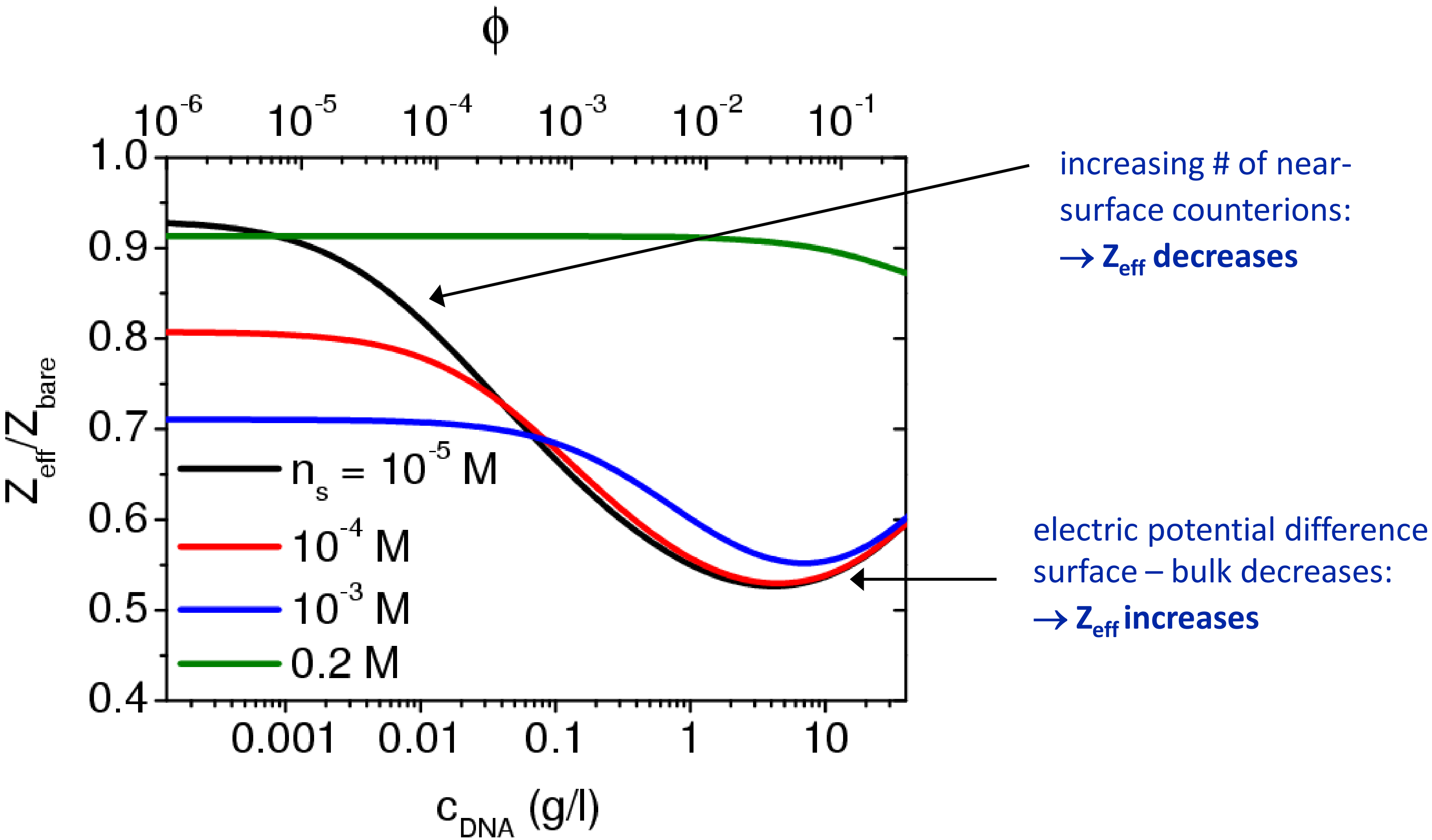
$$\kappa \rightarrow \kappa_{eff}$$

in DLVO potential (el. part)



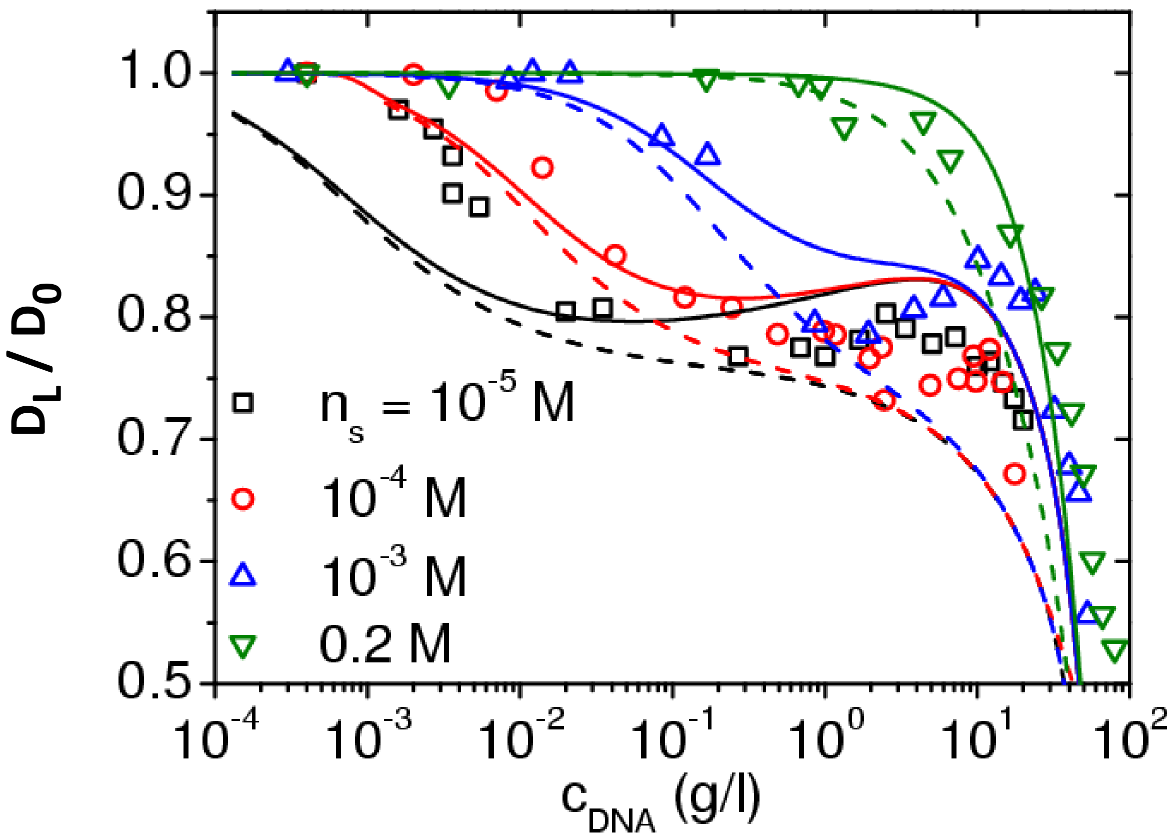
Prienagonda et al., JCP **126** (2007)

Concentration dependence of effective charge (spherical DNA fragment model)



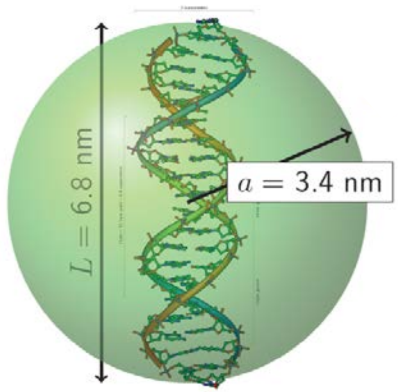
- Non - monotonic behavior of effective charge at low salinity

Simplified MCT with HI and charge - renormalization



Fragments modeled as spheres:

(a = 3.4 nm and Z = 42)



solid: with HI
dashed: without HI
symbols: exp. data

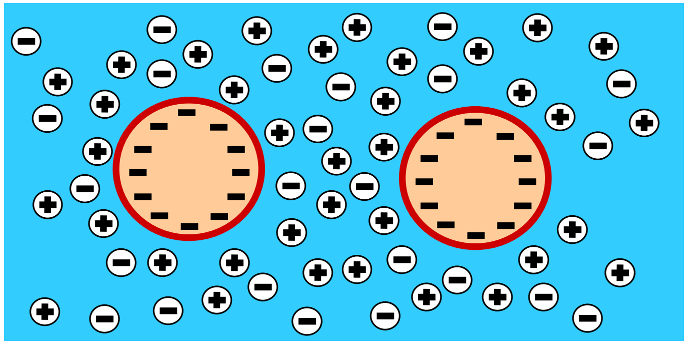
McPhie & Nägele, Phys. Rev. **78** (2008)

Non - monotonicity: concerted effect of colloid - colloid HI and charge renormalization

8. Primitive model electrokinetics

- Macroion long-time self-diffusion
- Electrolyte viscosity and conductivity

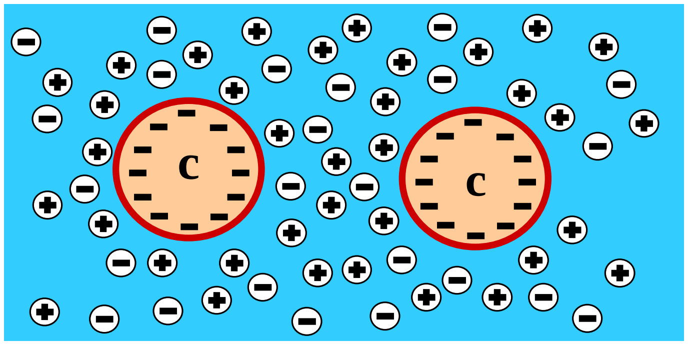
8.1 Macroion self-diffusion

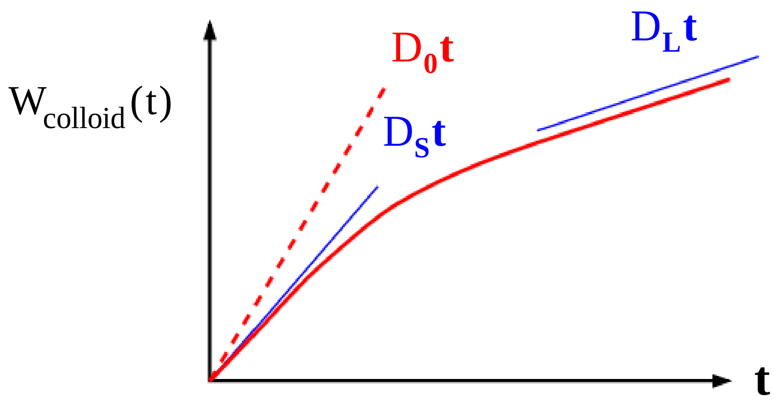


Electrolyte ion´s dynamic effect on d_L?

- All ions treated as charged hard spheres (dynamic Primitive Model)
- Account of RP far - field hydrodynamic interactions between all ionic species
- Simplified mode - coupling theory (MCT) for ionic mixtures

Electrolyte versus colloid friction





→ **Input in theory**: partial PM static structure factors $S_{cc}(q) = S(q)$, $S_{c\pm}(q)$, $S_{+-}(q)$, …

$$D_L(\phi) = \frac{k_B T}{6\pi a \eta_0 \left[1 + \Delta\zeta^{EF}(\phi) + \Delta\zeta^{CF}(\phi)\right]}$$

$$\Delta\zeta^{CF}(\phi = 0) = 0$$

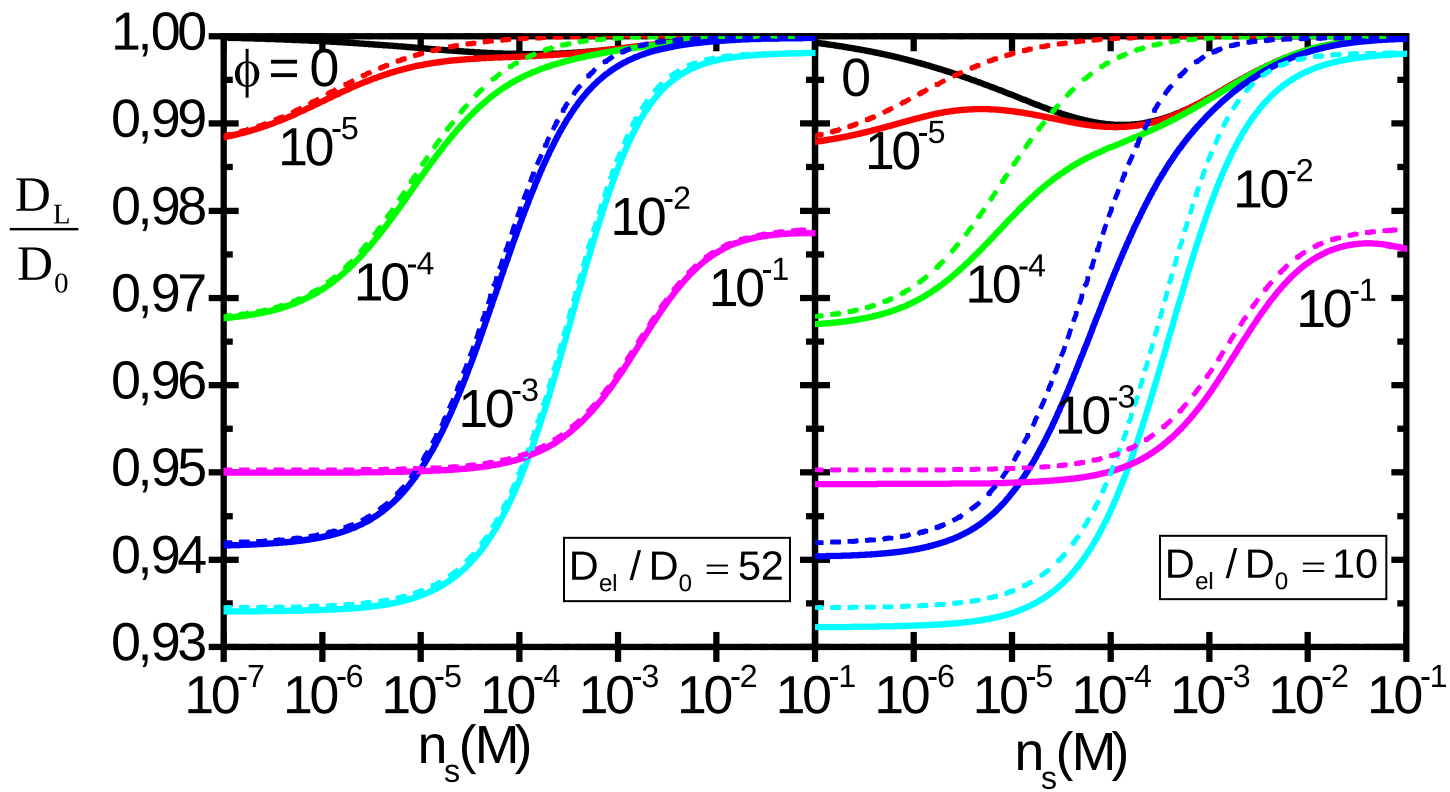
electrolyte friction : all PM $S_{\alpha\beta}(q)$'s

colloid friction : $S(q)$

(delayed microion relaxation)

Simplified MCT results: electrolyte versus colloid friction

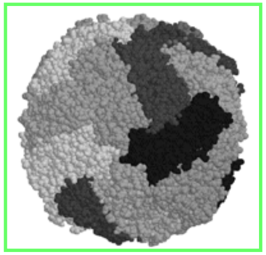
$$\frac{D_L}{D_0} = \frac{1}{1 + \Delta\zeta^{EF}(\phi) + \Delta\zeta^{CF}(\phi)}$$



Apoferritin:

$Z = 10$

$a = 6.9$ nm



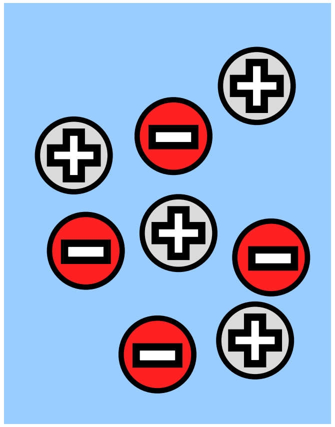
dashed: CF only
solid: EF & CF

McPhie & Nägele
J. Chem. Phys. **127**, 2007

- Dynamic influence of electrolyte ceases with increasing ϕ (**homogenized** background)

8.2 Electrolyte viscosity and conductivity

- Primitive Model & Smoluchowski dynamics treatment
- Inclusion of ion - ion HI for short-time **and** relaxation parts of transport coefficients



$$\eta - \eta_0 = \Delta\eta_\infty + \Delta\eta$$

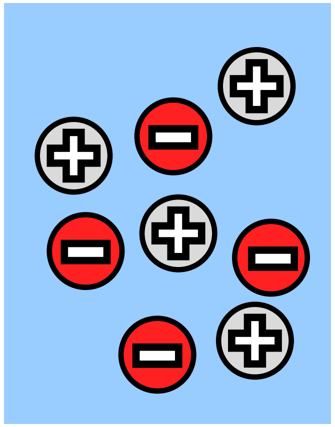
$$\Delta\eta = \int_0^\infty dt \int d^3q \, \mathrm{Tr}\left[\mathbf{U}(q,t)^2\right]$$ multispecies MCT **with HI**

$$\mathbf{U}(q,t) = \left[\mathbf{V}^{pot}(q,t) + \mathbf{V}^{hyd}(q,t)\right] \cdot \mathbf{S}^{-1}(q) \cdot \mathbf{F}(q,t) \cdot \mathbf{S}^{-1}(q)$$

$$\{g_{++}(r),\ g_{--}(r),\ g_{+-}(r)\}$$ **only input (use MSA here for simplicity)**

$$\mathbf{F}(q,t) \approx \mathbf{F}_S(q,t) = \sum_{\alpha=1}^{m} \mathbf{\Lambda}_\alpha(q) e^{-\lambda_\alpha(q)t}$$ m - mode short - time approximation as input

Falkenhagen - Onsager limiting laws recovered for point ions and $n_T < 0.01$ M



$$\kappa \propto \sqrt{n_T}$$

- ions with equal diffusion coefficient d_0

$$\Delta\eta = \frac{k_B T \kappa}{480\,\pi\, D_0}\left[1 + 0.72 \times \frac{D_\kappa}{D_0} + O\left(\kappa^2\right)\right]$$

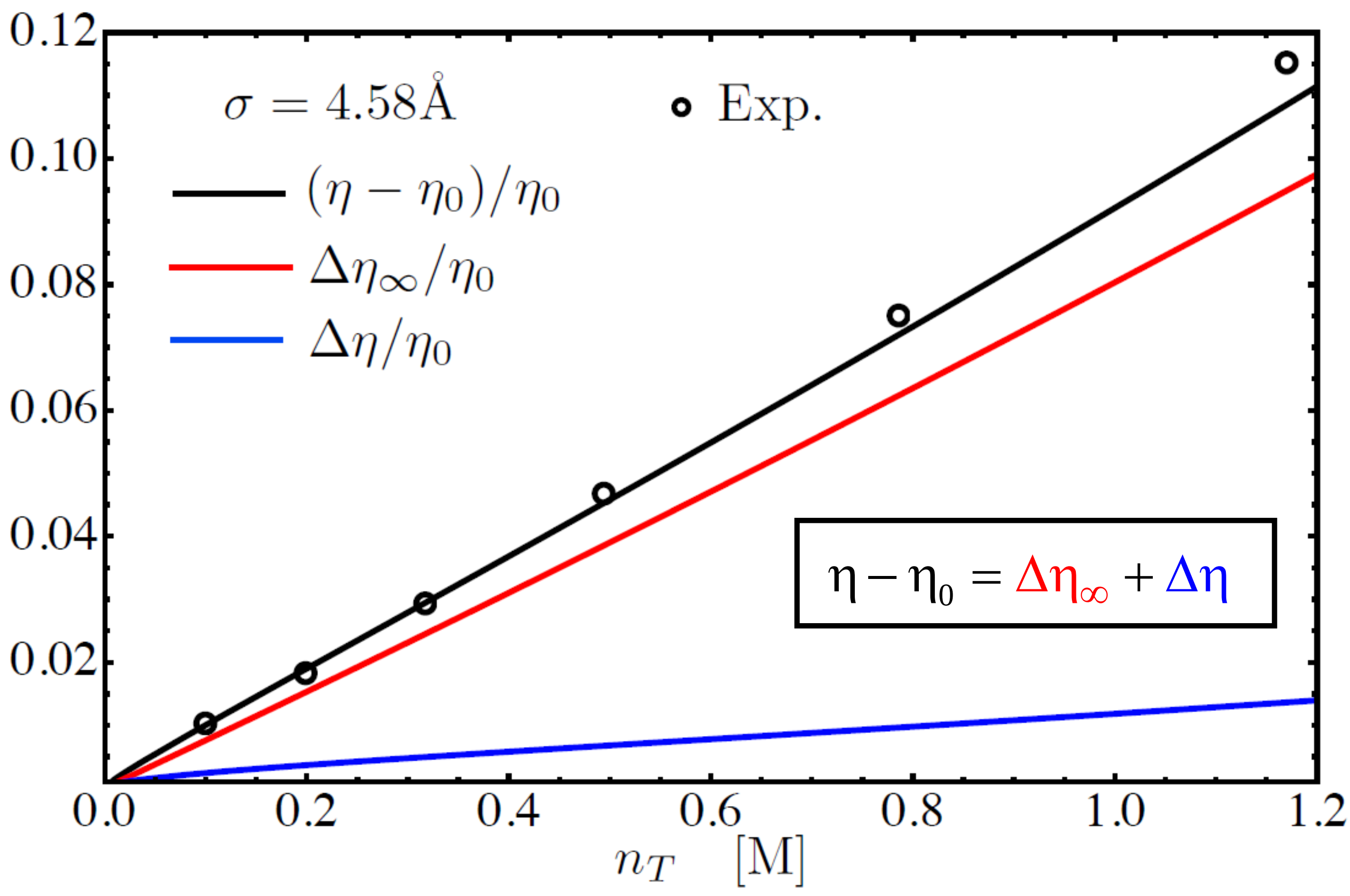
HI contribution (leading order)

$$D_\kappa = \frac{k_B T}{6\,\pi\,\eta_0}\kappa \ll D_0$$

- Analytic MCT viscosity expression obtained for equal - sized ions

C. Contreras-Aburto and G. Nägele, J. Phys.: Condens. Matter **24**, 464108 (2012)

Viscosity η of 1:1 electrolyte (NaCl in water)



$$\sigma = a^{hyd}_{Na^+} + a^{hyd}_{Cl^-}$$

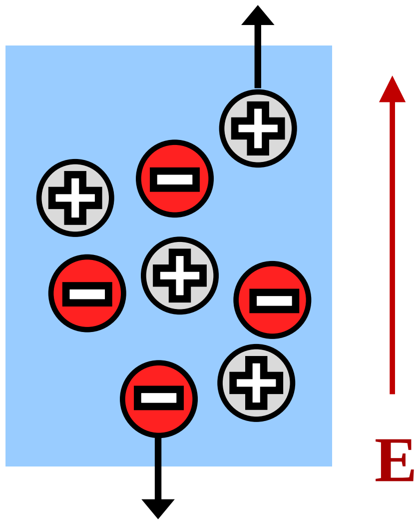
- Good viscosity description without adjustable parameters

Contreras-Aburto and Nägele, submitted (2013)

Simplified MCT calculation of molar conductance Λ

- Zero mean suspension velocity frame: Ohm's law

$$\left\langle \mathbf{j}_{el} \right\rangle_{stat} = n_T \, \Lambda \, \mathbf{E} = n_T \left(e^2 \sum_{\alpha=1}^{m} x_\alpha \, z_\alpha \, \mu_\alpha^{el} \right) \mathbf{E}$$



$$\left\langle \mathbf{v}_\alpha \right\rangle_{stat} = \mu_\alpha^{el} \, e \, \mathbf{E}$$

electrophoretic ion - mobilities

$$\Lambda = -e^2 \lim_{t\to\infty} \lim_{q\to 0} \frac{1}{q^2} \frac{\partial}{\partial t} F_{ZZ}(q,t)$$

$$F_{ZZ}(q,t) = \sum_{\alpha,\beta=1}^{m} \left(x_\alpha x_\beta \right)^{1/2} z_\alpha z_\beta F_{\alpha\beta}(q,t)$$

charge fluctuation dynamic structure factor

- All conduction-diffusion properties expressable in terms of partial long-time mobilities

$$\mu^{L}_{\alpha\beta} = -\lim_{t\to\infty}\lim_{q\to 0}\frac{1}{q^2}\frac{\partial}{\partial t}F_{\alpha\beta}(q,t)$$

mobility coefficients ($\propto$ **Onsager coefficients**)

$$k_B T \boldsymbol{\mu}^{L} = \mathbf{m}\cdot\left[\mathbf{1}+\mathbf{H}^{-1}\cdot\mathbf{m}\right]^{-1}$$

- many – species MCT with HI

$$m_{\alpha\beta} = \lim_{q\to 0}\int_0^\infty dt\, M^{c}_{\alpha\beta}(q,t)$$

- simplification using $\mathbf{F}_S(q,t)$ as memory functions input

- Analytic MCT expression for symmetric binary electrolyte:

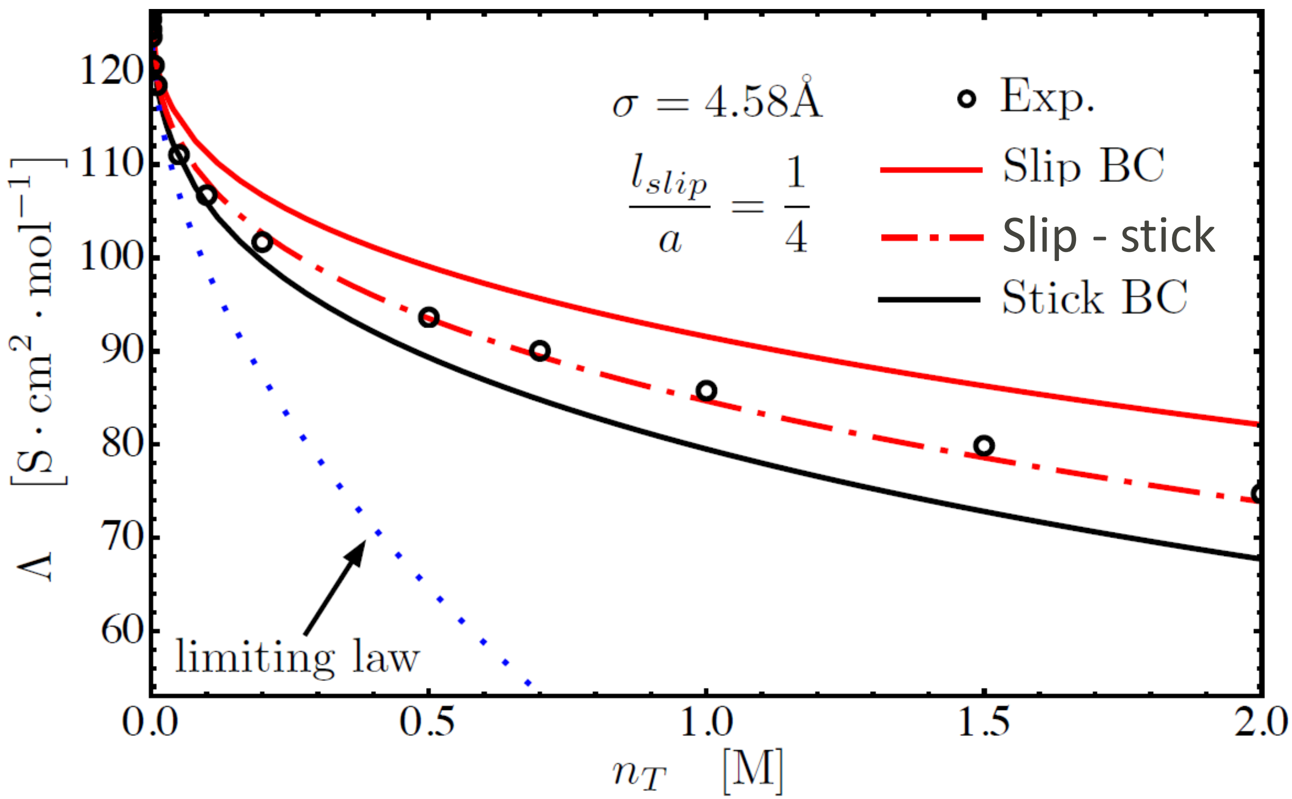
$$\Lambda = \left(\frac{H_{ZZ}/D_S}{H_{ZZ}/D_S + m^{(n)}}\right)\Lambda_S$$

charge - fluctuation hydrodynamic function

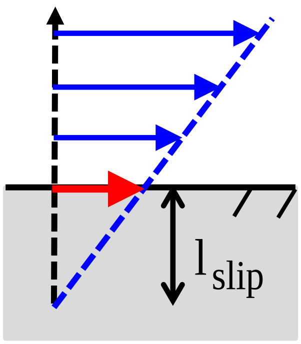
relaxation effect (by MCT)

$$\Lambda < \Lambda_S = \left(H_{ZZ}/D_S\right)\Lambda_0$$

Molar conductance Λ of 1:1 electrolyte (NaCl in water)



$$\langle \mathbf{j}_{el} \rangle_{stat} = n_T \, \Lambda \, \mathbf{E}$$



- Good agreement at lower n_T for stick BC
- Good agreement at larger n_T for Navier mixed slip - stick BC HI
- Onsager - Fuoss limiting law recovered for $n_T < 0.01$ M

Contreras-Aburto and Nägele submitted (2013)