Colloidal Hydrodynamics

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Literature

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2. W.B. Russel, D.A. Saville, and W.R. Schowalter, ***Colloidal Dispersions***, Cambrigde University Press (1989)
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10. J. Mewis and N.J. Wagner, ***Colloidal Suspension Rheology***, Cambrigde University Press (2012)
11. G. Nägele***, Colloidal Hydrodynamics***, Manuscript in preparation (2012)

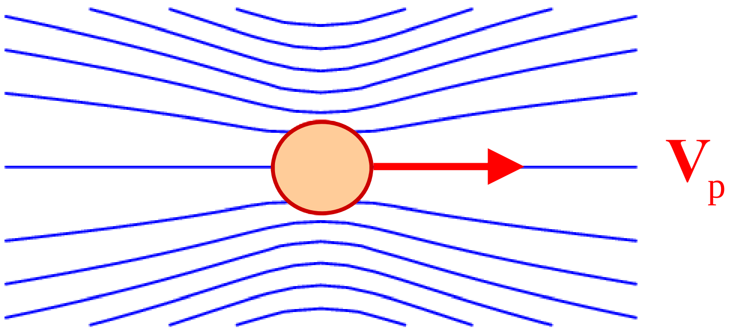
Content

1. Motivation

- Low Reynolds number flow
- Hydrodynamic Interaction (HI)
- Inertia – free particle dynamics

1.1 Low - Reynolds number flow

- Inertial forces tiny as compared to friction forces: **Reynolds - # << 1**
- Laminar fluid flow (kinematic reversibility): linear force – velocity relations
- Quasi-**inertia-free** motion of colloids / microorganisms *and* solvent (**Stokesian dyn.**)

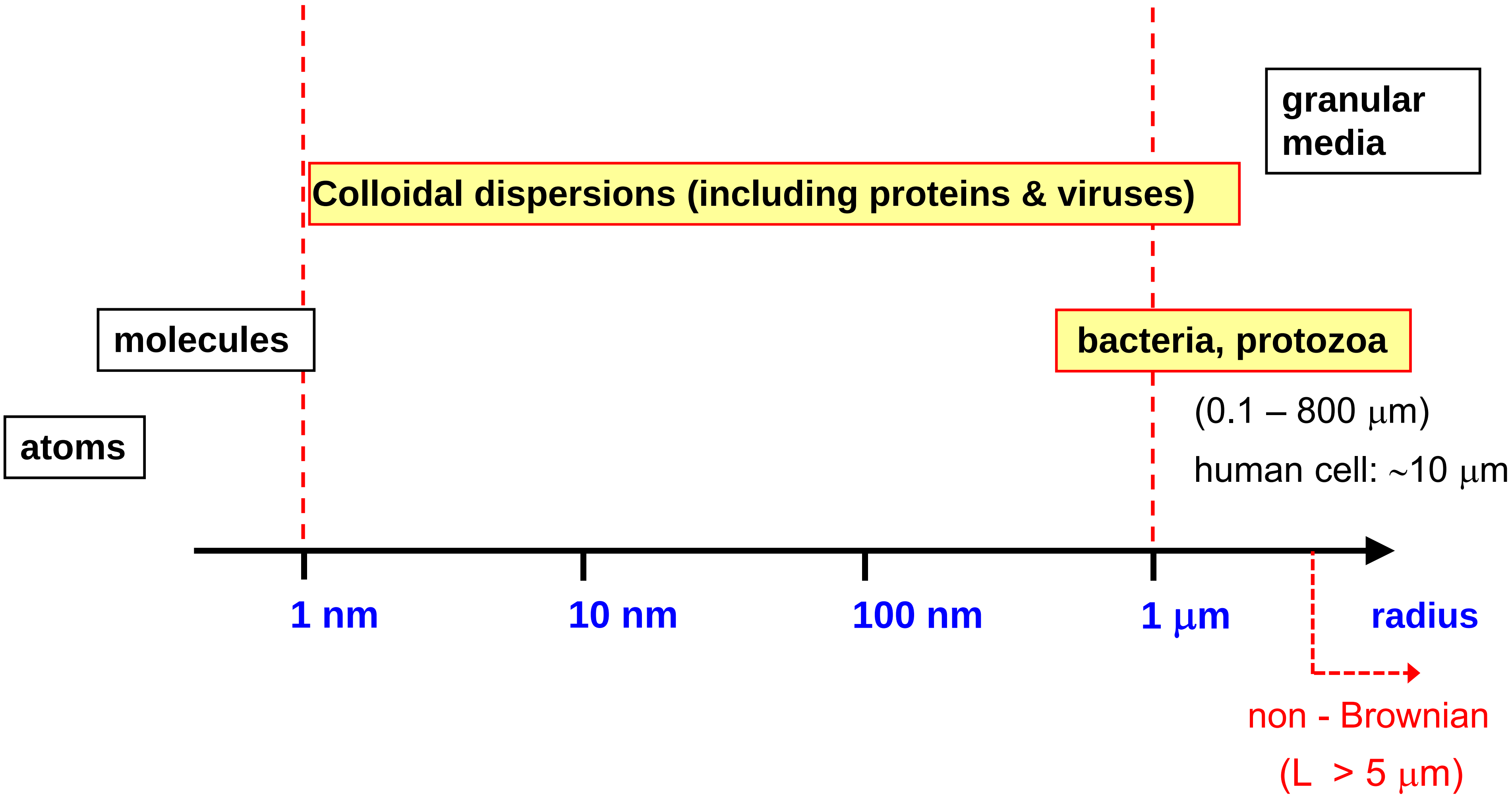


$$Re = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{\rho_f \, a V_p}{\eta_0}$$

in water:

wale:	10^8
human swimmer:	10000
gold fish:	100
colloid particle:	0.0001
bacteria /cells:	0.00001

Re << 1: colloids / microbes in water or macroscopic bodies in glycerine



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

Single sphere translating in quiescent fluid

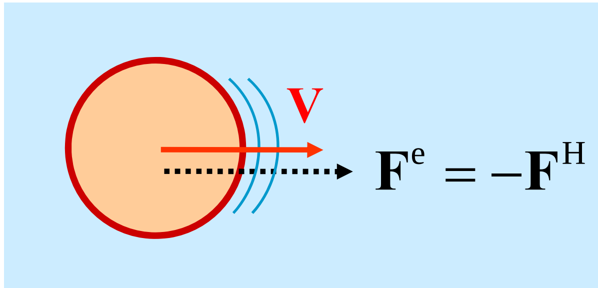
- **Sphere with stick (no-slip) BC ín quiescent infinite fluid**

$$\boxed{\mathbf{V} = \mu_0\, \mathbf{F}^e}$$

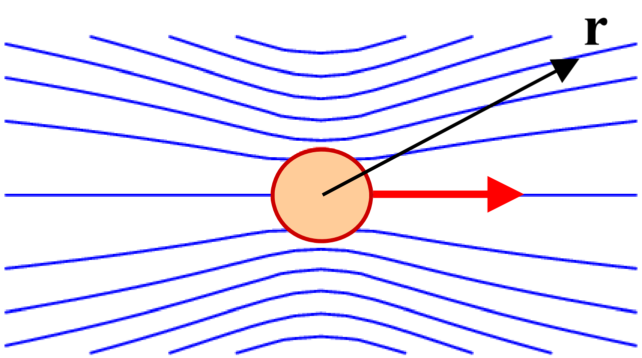
translational mobility

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

(6π → 4π : perfect slip)



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



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

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

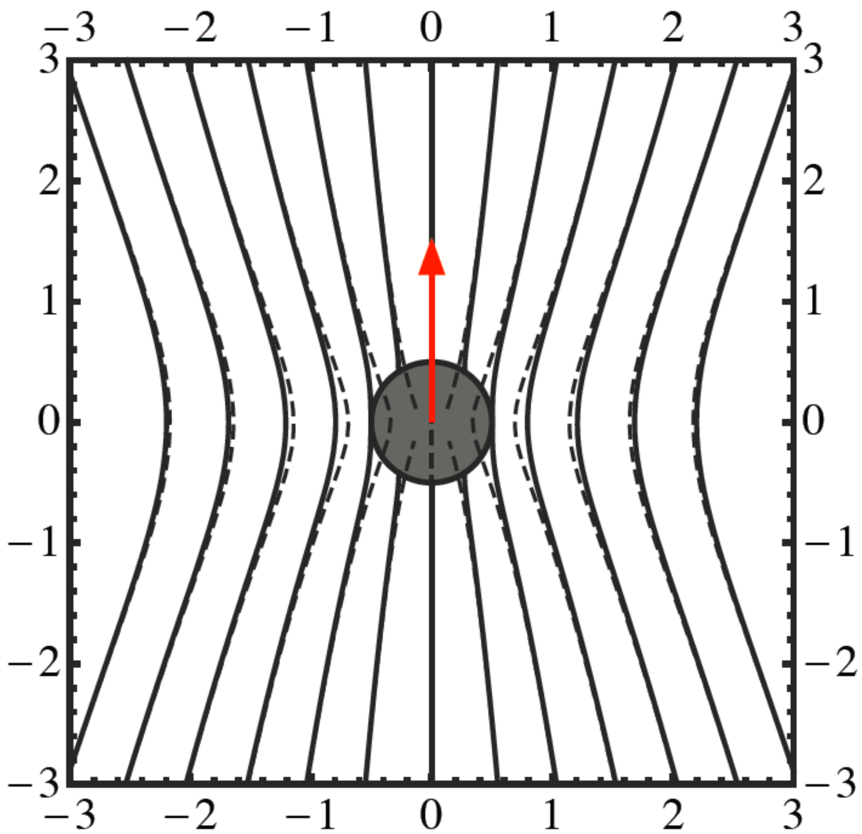
long-range decay

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

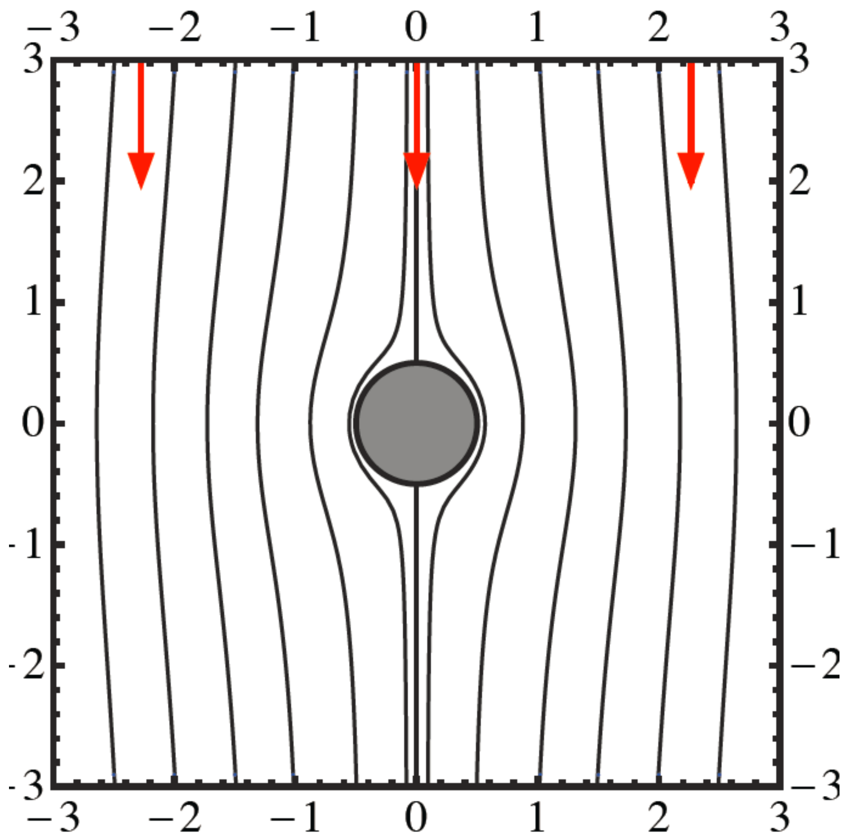
stream lines = path lines when stationary flow

- Sphere in quiescent, infinite fluid, stick BC
- Sphere stationary (rest frame)

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

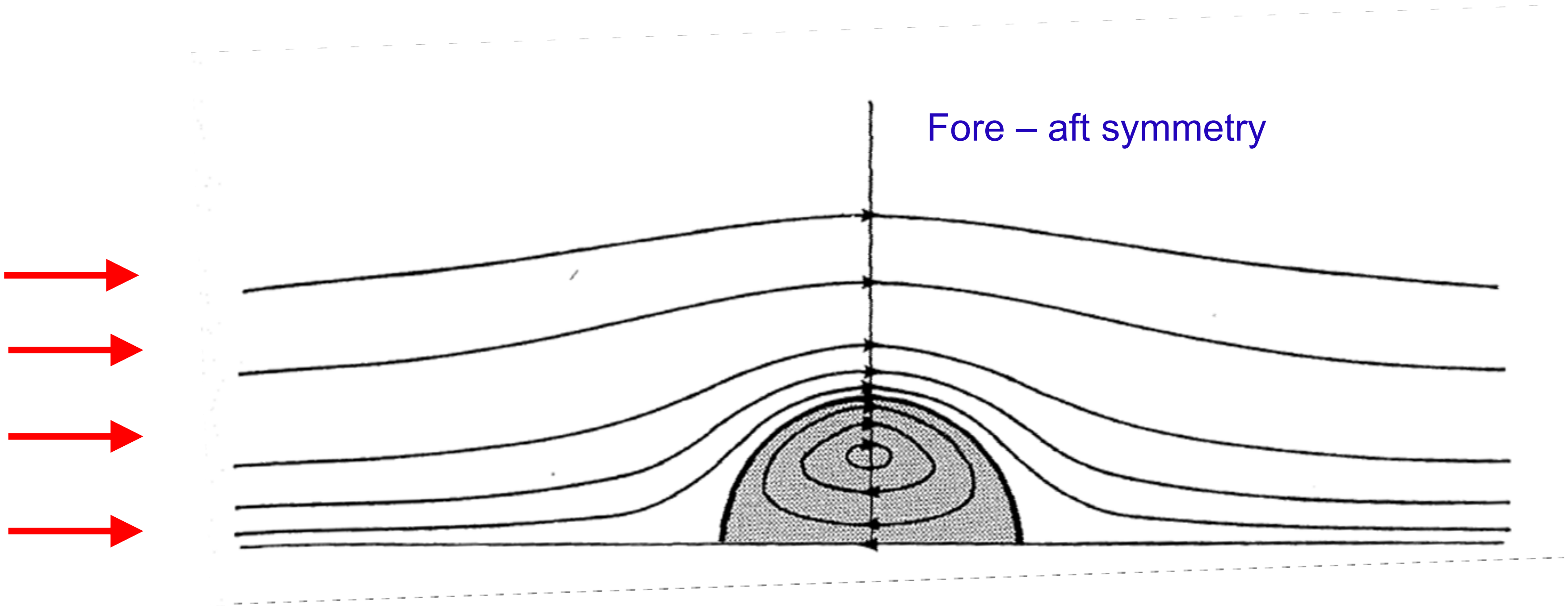


$\mathbf{u}_\infty = -\mathbf{V}$



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

- Flowlines inside and outside a stationary spherical droplet in a non-quiescent viscous fluid



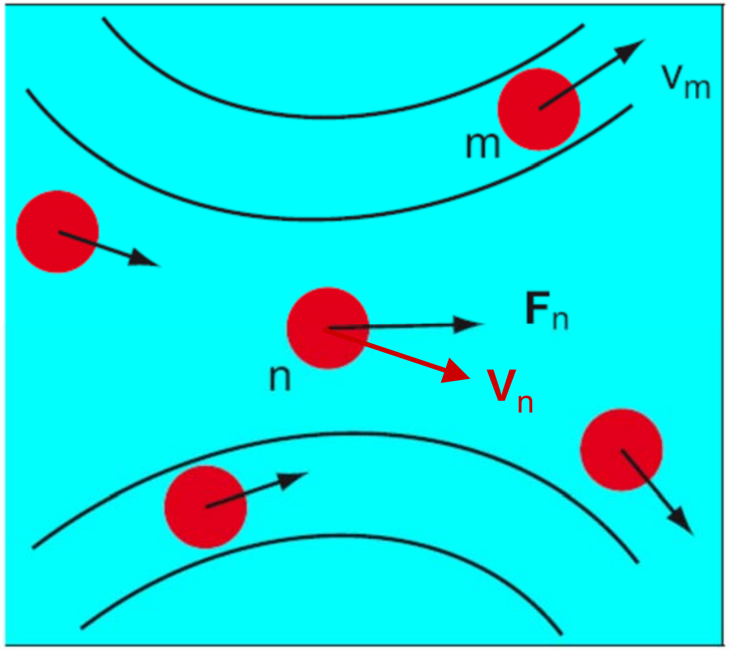
$$\mathbf{u}_\infty = \mathbf{V}$$

$$\mathbf{u}_\mathrm{i}(a\hat{\mathbf{r}})\cdot\hat{\mathbf{n}} = \mathbf{u}_\mathrm{a}(a\hat{\mathbf{r}})\cdot\hat{\mathbf{n}} = 0 \qquad \hat{\mathbf{t}}\cdot\boldsymbol{\sigma}_\mathrm{i}(a\hat{\mathbf{r}})\cdot\hat{\mathbf{n}} = \hat{\mathbf{t}}\cdot\boldsymbol{\sigma}_\mathrm{a}(a\hat{\mathbf{r}})\cdot\hat{\mathbf{n}}$$

$$\mathbf{u}_\mathrm{i}(a\hat{\mathbf{r}})\cdot\hat{\mathbf{t}} = \mathbf{u}_\mathrm{a}(a\hat{\mathbf{r}})\cdot\hat{\mathbf{t}}$$

Air bubble in fluid: zero tangential stress

1.2 Hydrodynamic Interaction

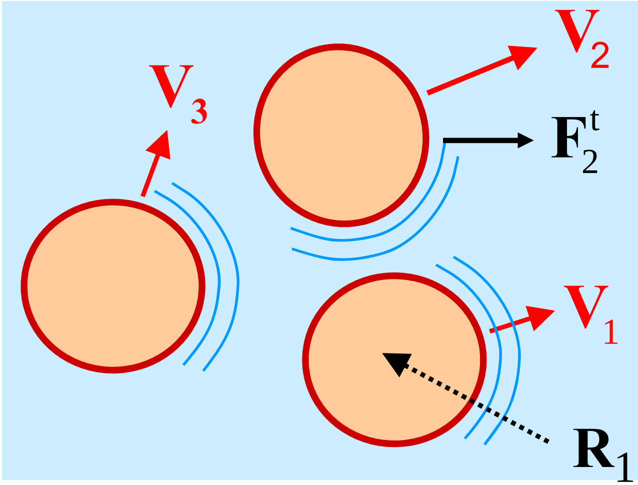


- V_n in general non - parallel to F_n but linear relation
- Instantaneous restructuring of flow profile around moving particles
- Long – range interaction non – pairwise additive

- **N freely rotating spheres in quiescent fluid: generalized Stokes law**

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

translational 3×3 mobility tensors



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

$$F = \zeta(X)\cdot V$$ friction problem

$$\zeta(X)\cdot\mu^{tt}(X) = 1$$

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

diffusivity matrix

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

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

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

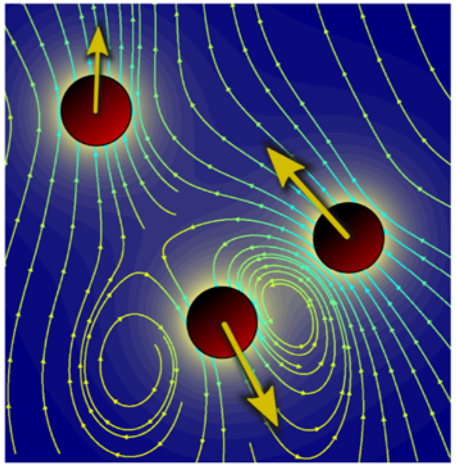
$$X = \{\mathbf{R}_1,\ldots,\mathbf{R}_N\}$$

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

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

3N x 3N matrix
symmetric & pos. definite

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



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

$$D_S = \frac{k_B T}{3} \mathrm{Tr} \left\langle \boldsymbol{\mu}_{11}^{tt} \right\rangle$$

- self-diffusion coefficient $\boldsymbol{\mu}_{11}^{tt} \sim O(r^{-4})$

$$\mathbf{V}_{sed} = \left\langle \sum_{p=1}^{N} \boldsymbol{\mu}_{1p}^{tt}(X) \right\rangle \cdot \mathbf{F}^e$$

- mean sedimentation velocity (**renormalization** required) $\boldsymbol{\mu}_{12}^{tt} \sim O(r^{-1})$

- $\langle \ldots \rangle$ average over homogeneous and isotropic particle ensemble

Inertia – free particle dynamics

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

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

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

"stopping distance"

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

Inertia – free particle dynamics

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

- pure configuration - space description for t $\gg \tau_B$

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

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

pdf

Irreversibility (Brownian motion ∝ T)

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

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

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

- Stokes – Liouville equation for **driven system** of non – Brownian particles (T – indep.):

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

$$P(X, t \to \infty) \to P_{stat}(X) \ \ ???$$

- **non-linear coupling: HI – mictostructure**
- **T - limit existent ?**

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

2. Examples of hydrodynamic effects

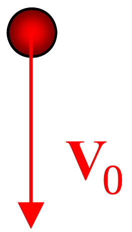
- Individual particle level
- Macroscopic transport properties

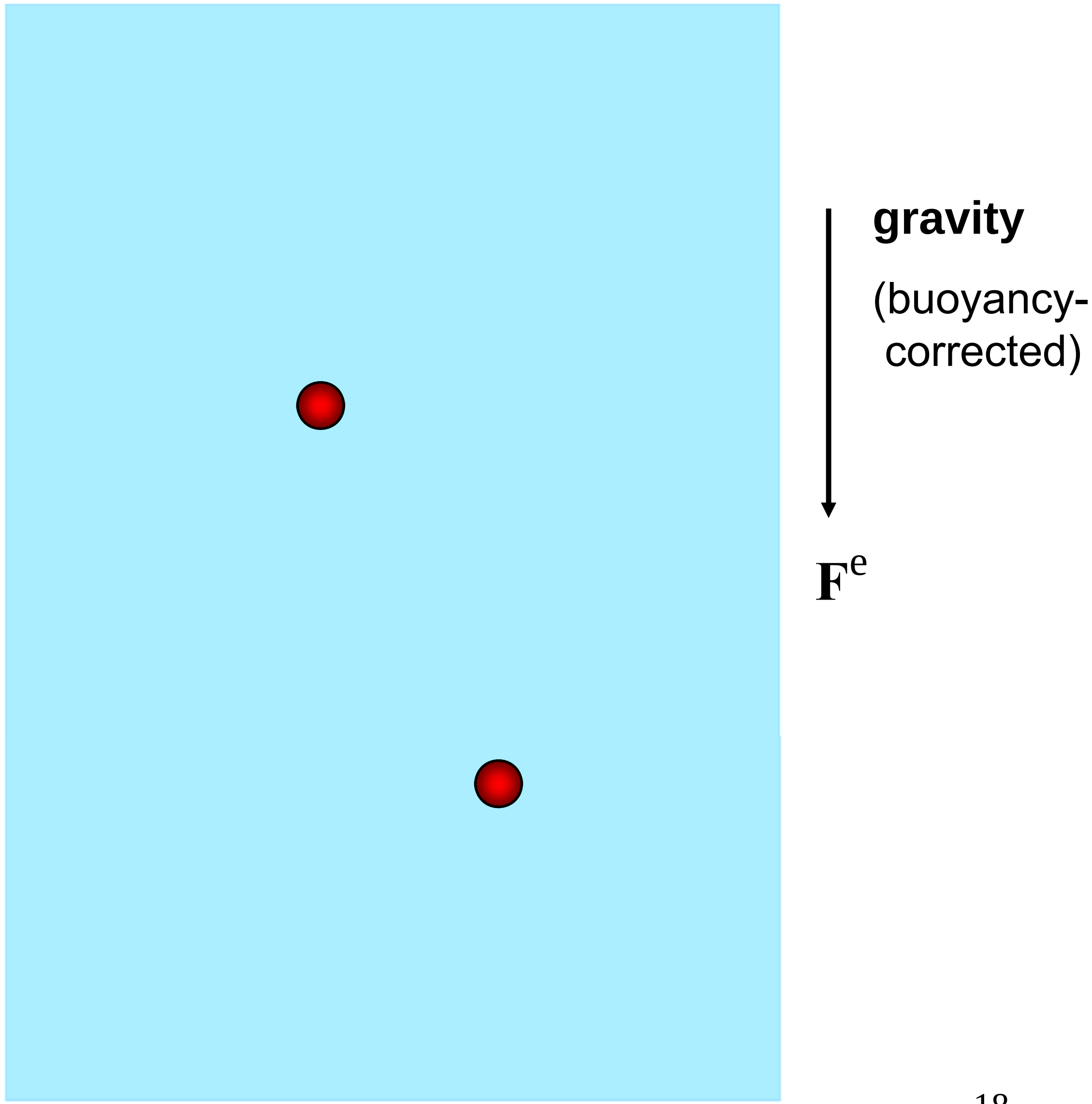
2.1 Examples: Individual particle level

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

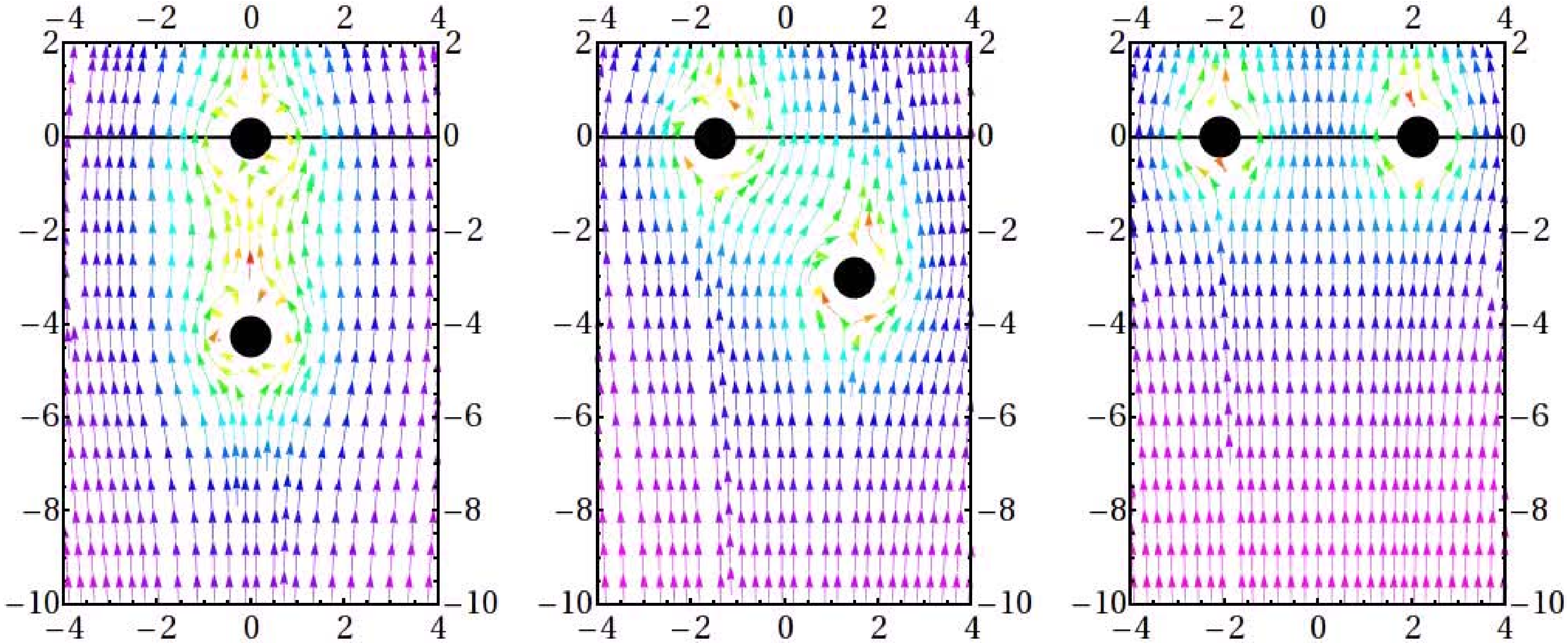
$$\mathbf{V}_0 = \mu_0 \mathbf{F}^e$$

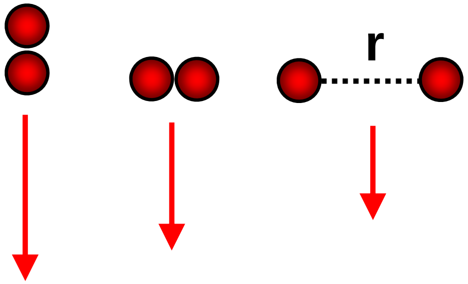
$$\mu_0^t = \frac{1}{6\pi\eta_0 a}$$





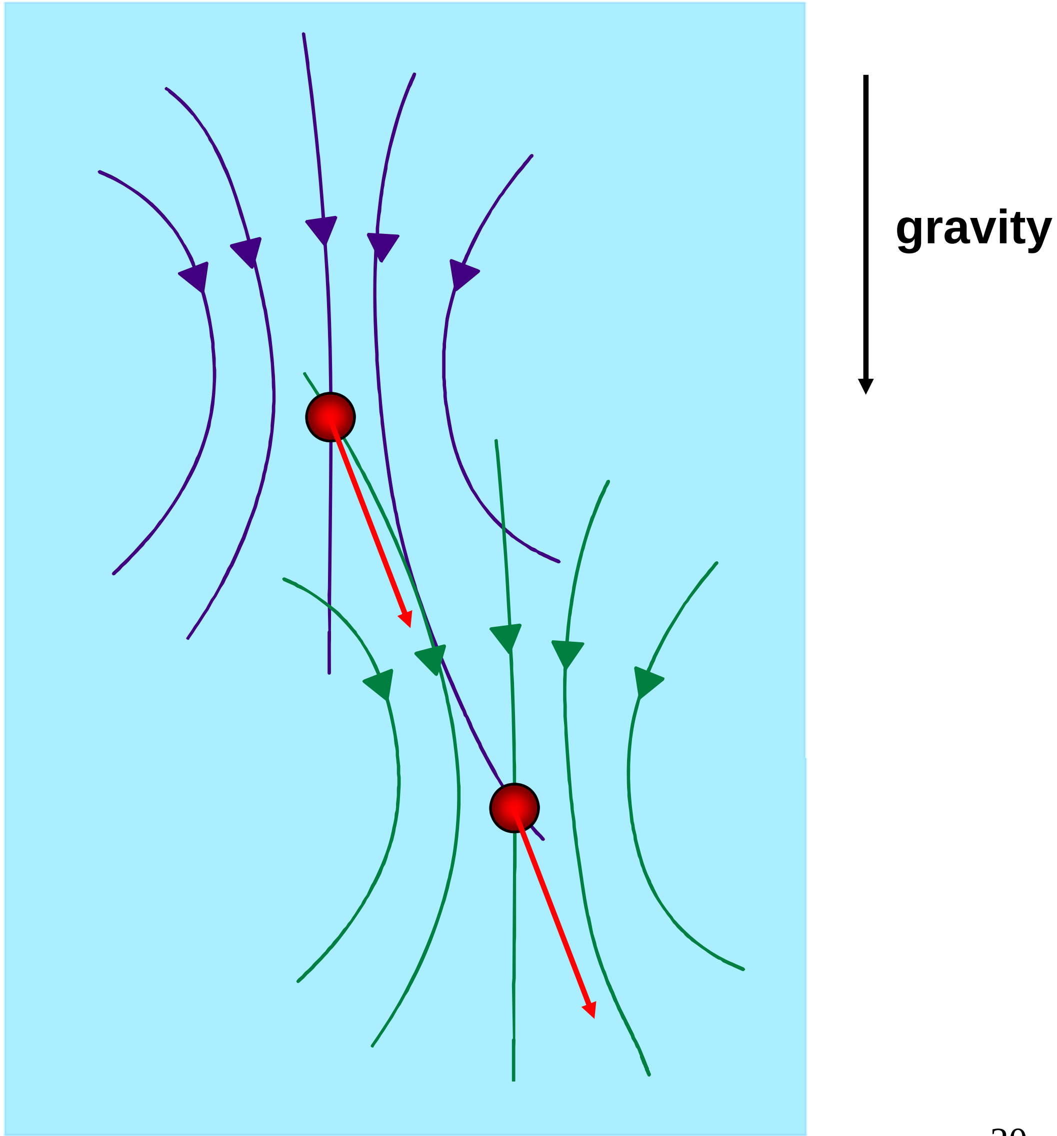
The sedimentation race: bet which pair settles fastest, and how ?





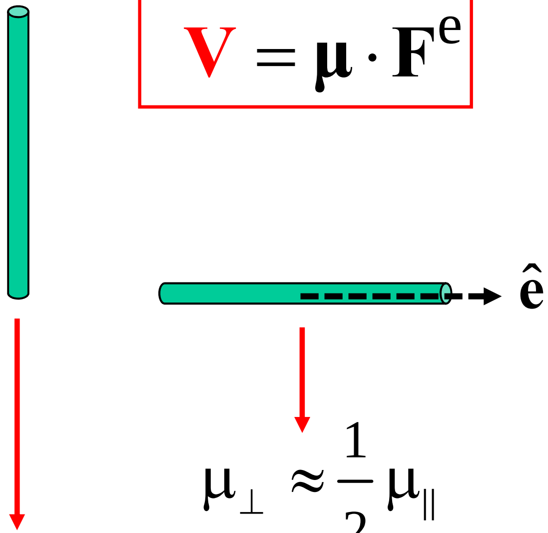
constant sep. vector **r**

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



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

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



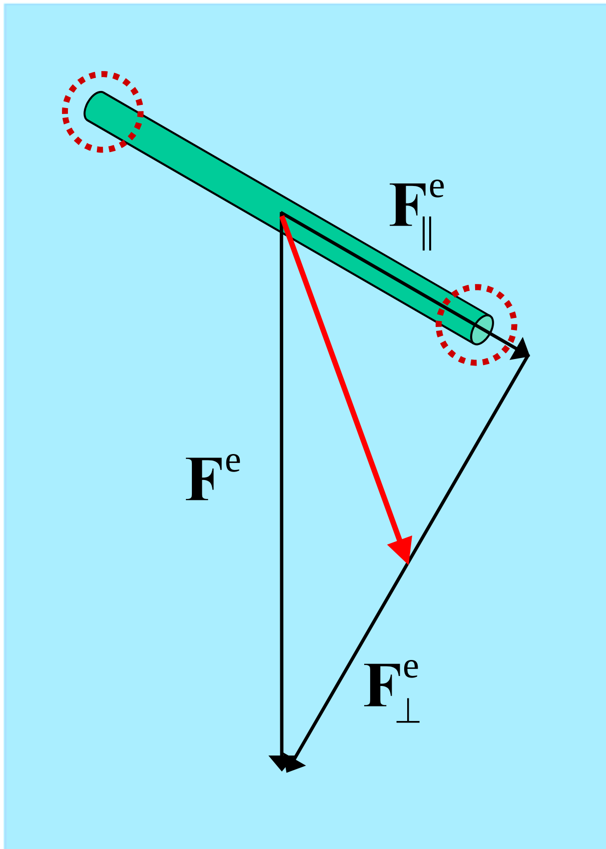
$$\mu_\perp \approx \frac{1}{2} \mu_{||}$$

(transl. mobilities for L >> D)

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

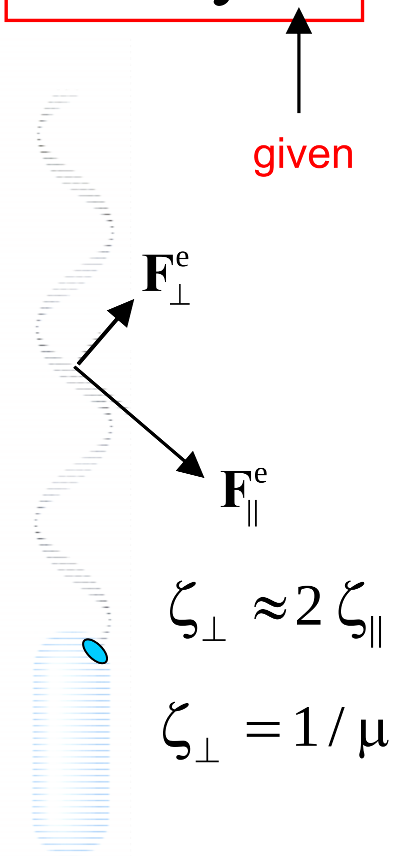
$$\mathbf{V} = \mu_{||} \mathbf{F}^e_{||} + \mu_\perp \mathbf{F}^e_\perp$$

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



Experiment: needle in syrup
no rotation

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

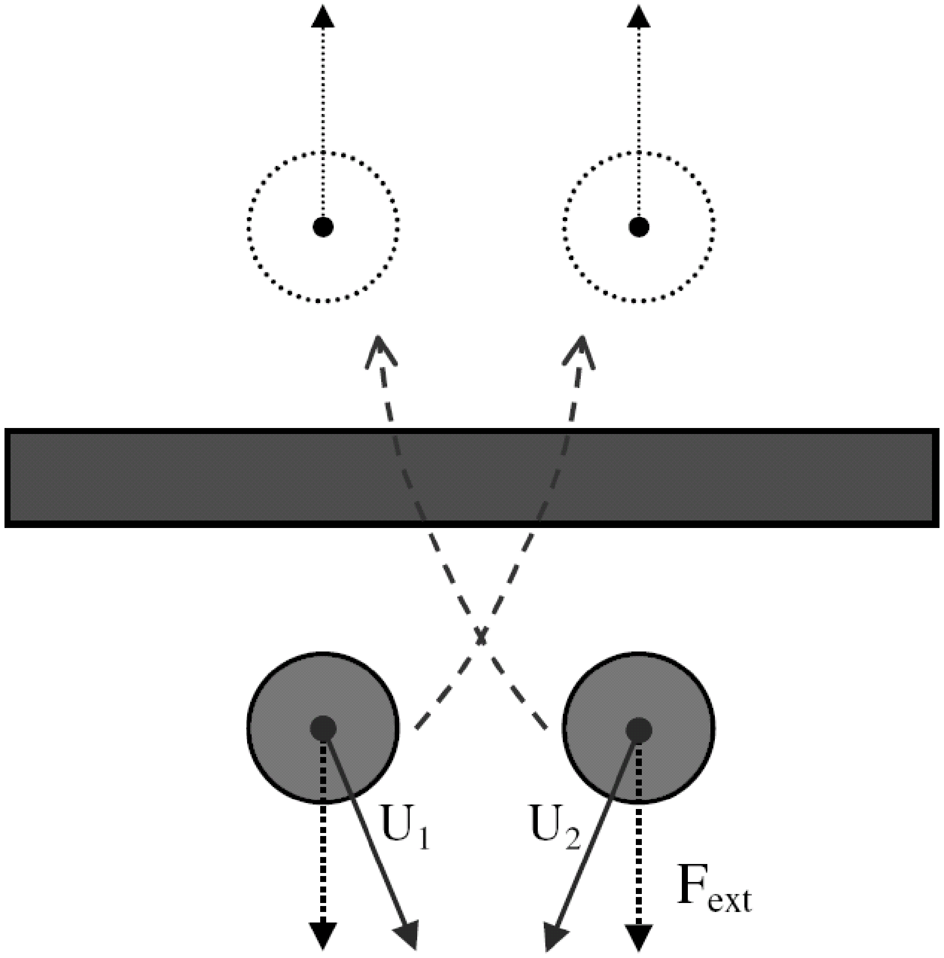


$$\zeta_\perp \approx 2\, \zeta_{||}$$

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

Flagella bundle:
HI synchronized

Apparent like - charge attraction of particles near boundary



Squires & Brenner, PRL (2000)

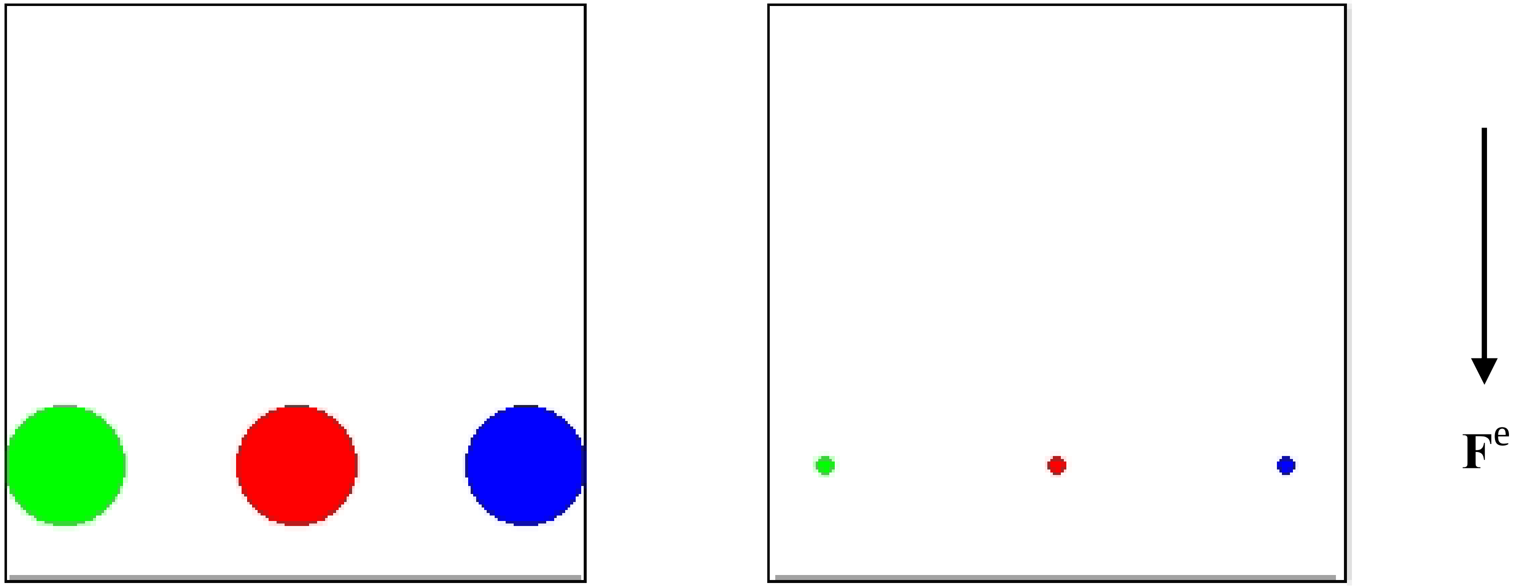
charged glass wall or
liquid - air interface

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

- Attractive wall: apparent repulsion

Sedimentation of 3 non-Brownian spheres: symmetric & planar start configuration

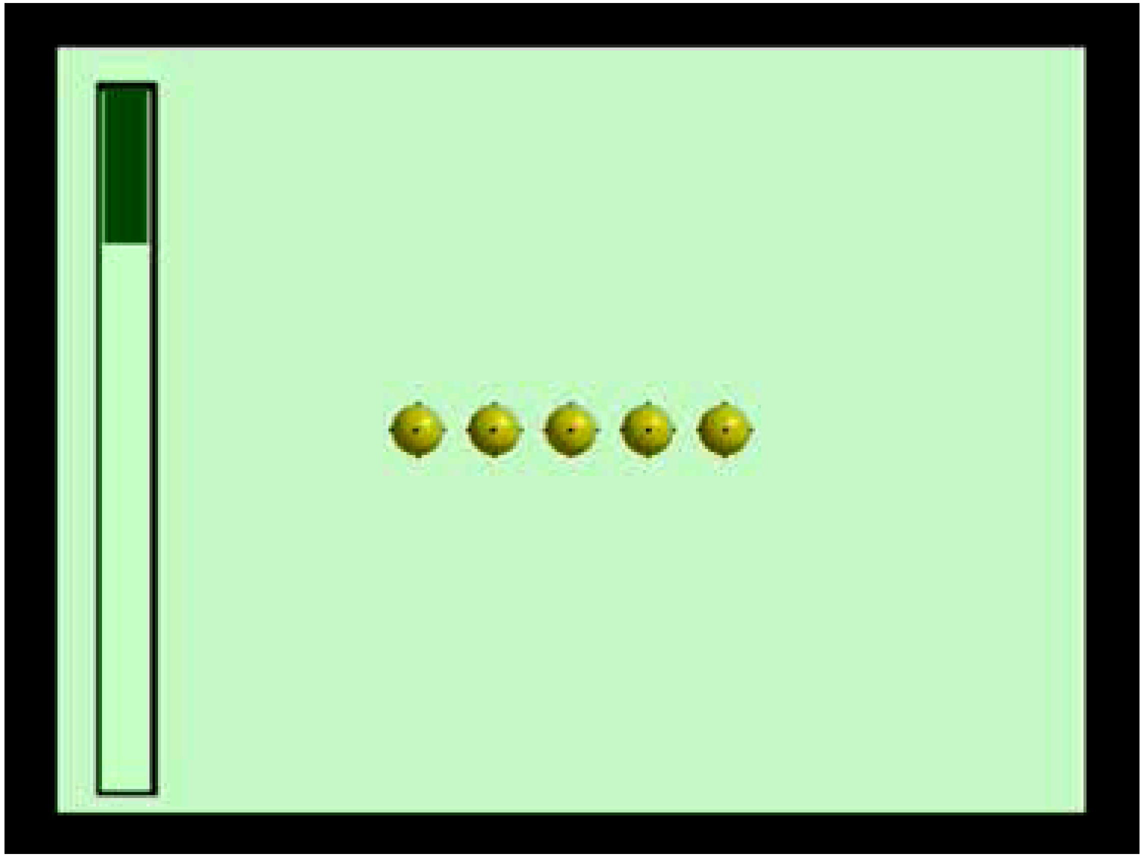
$$\frac{d}{dt}\mathbf{R}_i(t) = \left(\sum_{k=1}^{3} \boldsymbol{\mu}_{ik}^{tt}\left(X(t)\right) \right) \cdot \mathbf{F}^e$$



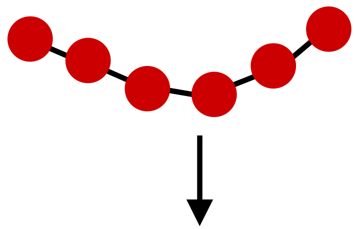
- **End of world**: point particles collapse on single point after finite time, acquire infinite velocity.
- **Spheres:** equilibrium configuration reached after infinite time, with pair of two upper spheres following lower one.

Courtesy: M. Ekiel-Jezewska & E. Wajnryb, Arch. Mech. **58**, 489 (2006)

Five non - Brownian spheres in equidistant start configuration

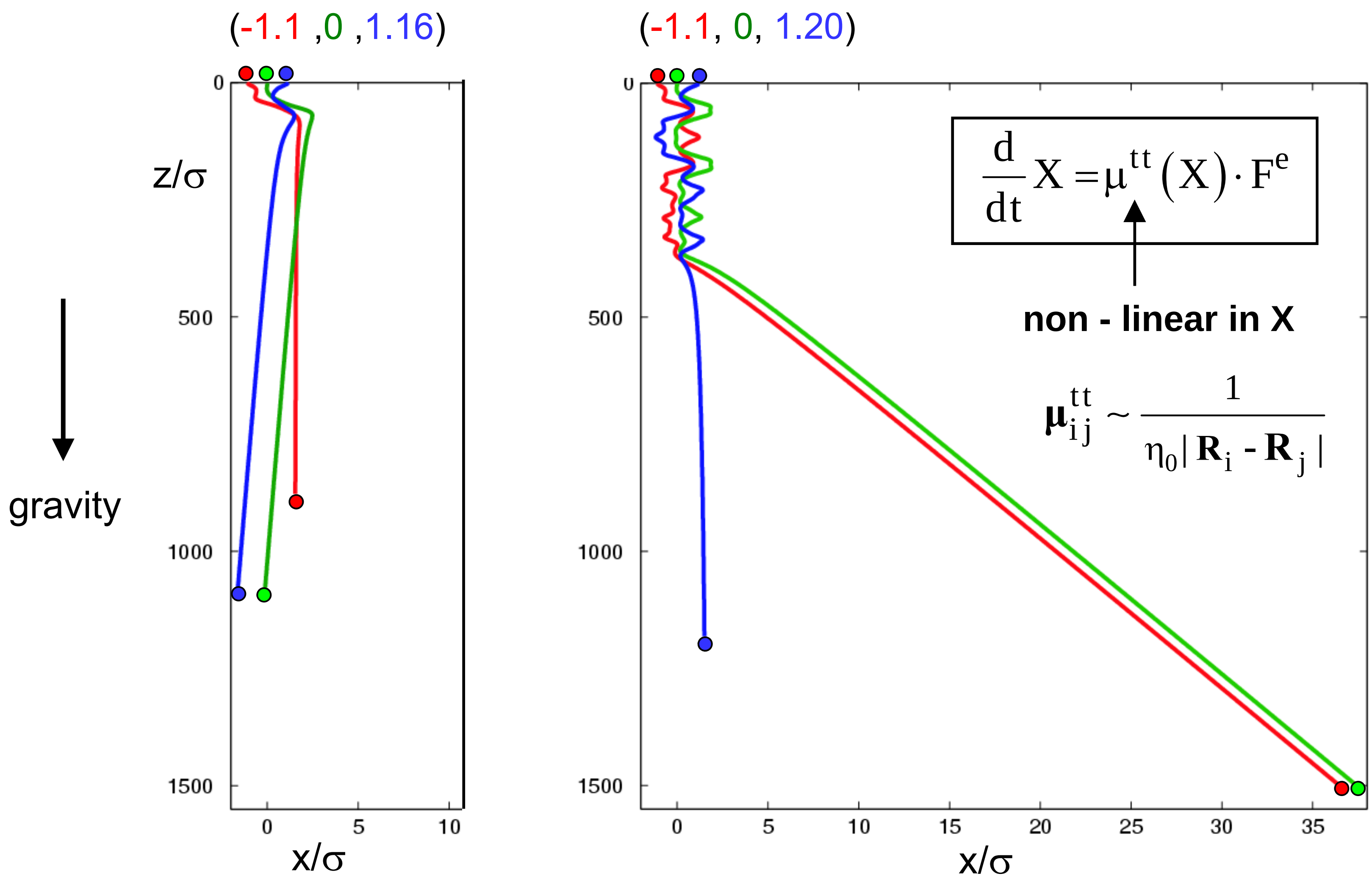


- pair distances are varying
- dimer formation: „kissing“
- sensitive dependence on initial conditions
- end - lagging of polymers



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

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



$$\frac{d}{dt}X = \mu^{tt}(X)\cdot F^{e}$$

$$\boldsymbol{\mu}_{ij}^{tt} \sim \frac{1}{\eta_0 |\mathbf{R}_i - \mathbf{R}_j|}$$

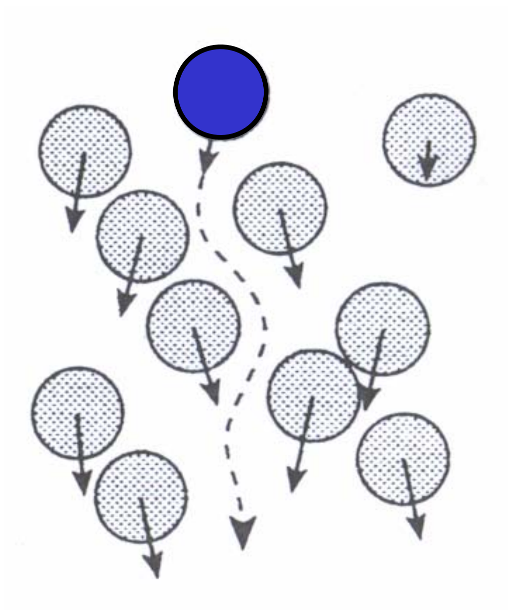
- Sensitive dependence on initial configuration for N > 2 → **chaotic trajectories**

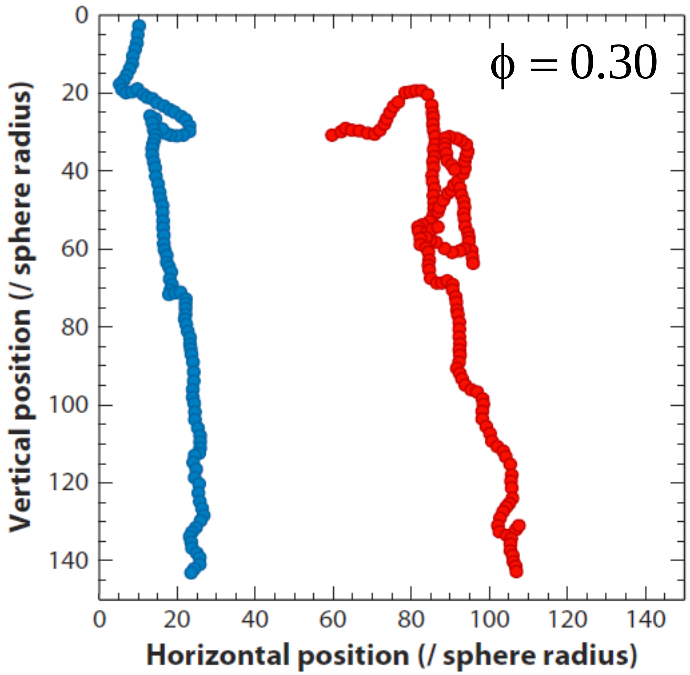
Courtesy: M. Ekiel-Jezewska & E. Wajnryb, Phys. Rev. E **83**, 067301 (2011)

Hydrodynamic „diffusion“ (mixing) due to many - body HI

- Sedimentation of index-matched non-Brownian glass beads

gravity



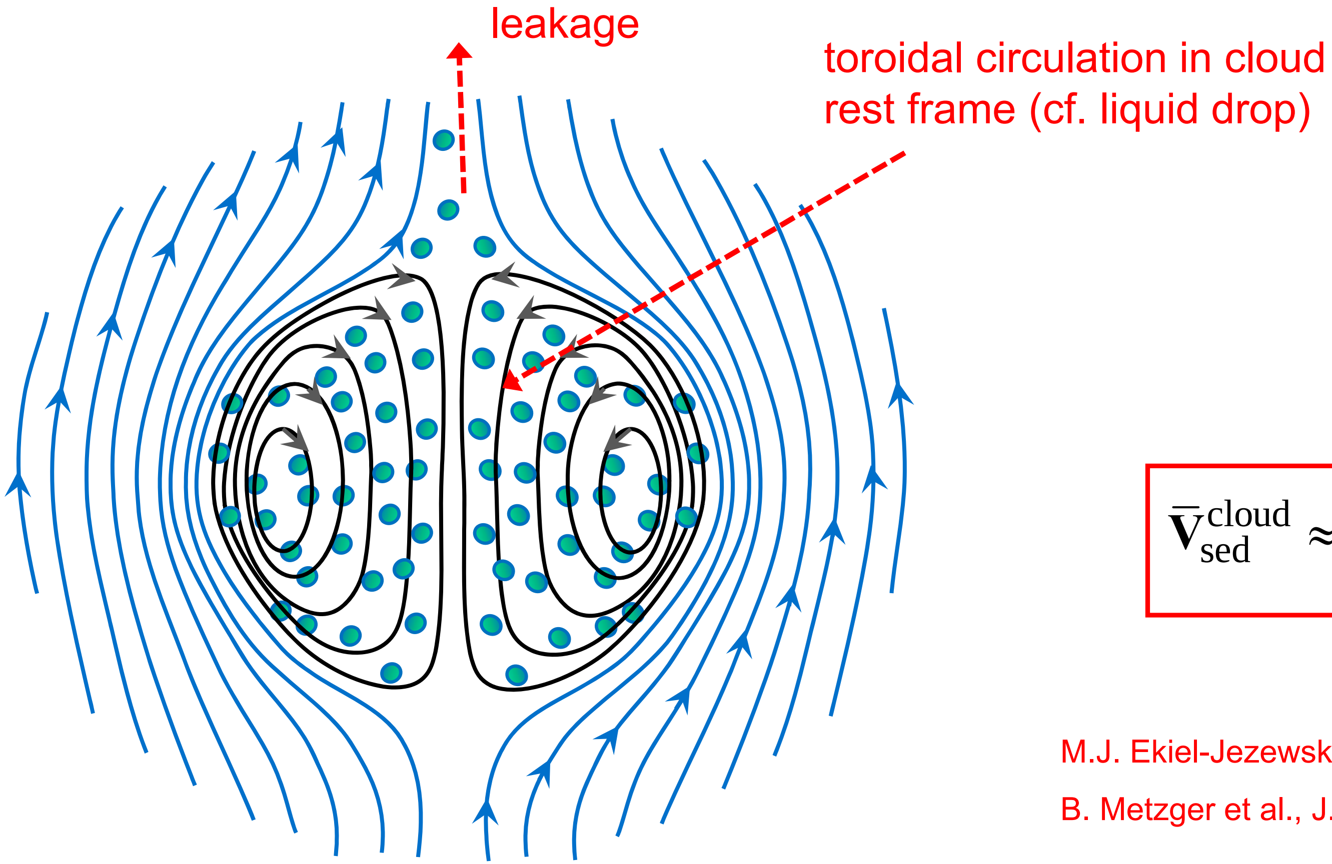


- driven, non-equilibrium system
- meandering trajectories & strongly fluctuating velocities
- particle migration across streamlines (mixing)
- existence & form of final stationary particle distribution $P_{stat}(X)$ still under debate
- slowly sedimenting colloidal particles $\rightarrow$ Brownian trajectories & $P_{stat}(X)$ existent

E. Guazzelli & J. Hinch

Annu. Rev. Fluid Mech. **43** (2011)

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



$$\mathbf{V}_{\mathrm{sed}}^{0} = \mu_0^{\mathrm{t}}\,\mathbf{F}^{\mathrm{e}}$$

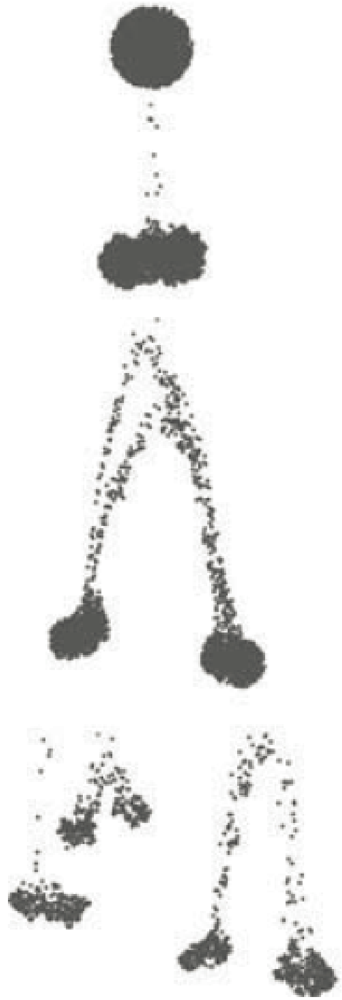
$$\bar{\mathbf{V}}_{\mathrm{sed}}^{\mathrm{cloud}} \approx \mathbf{V}_{\mathrm{sed}}^{0} + \frac{N-1}{5\pi\eta_0 R}\,\mathbf{F}^{\mathrm{e}}$$

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)

- Point - particle simulation
  (N = 3000)

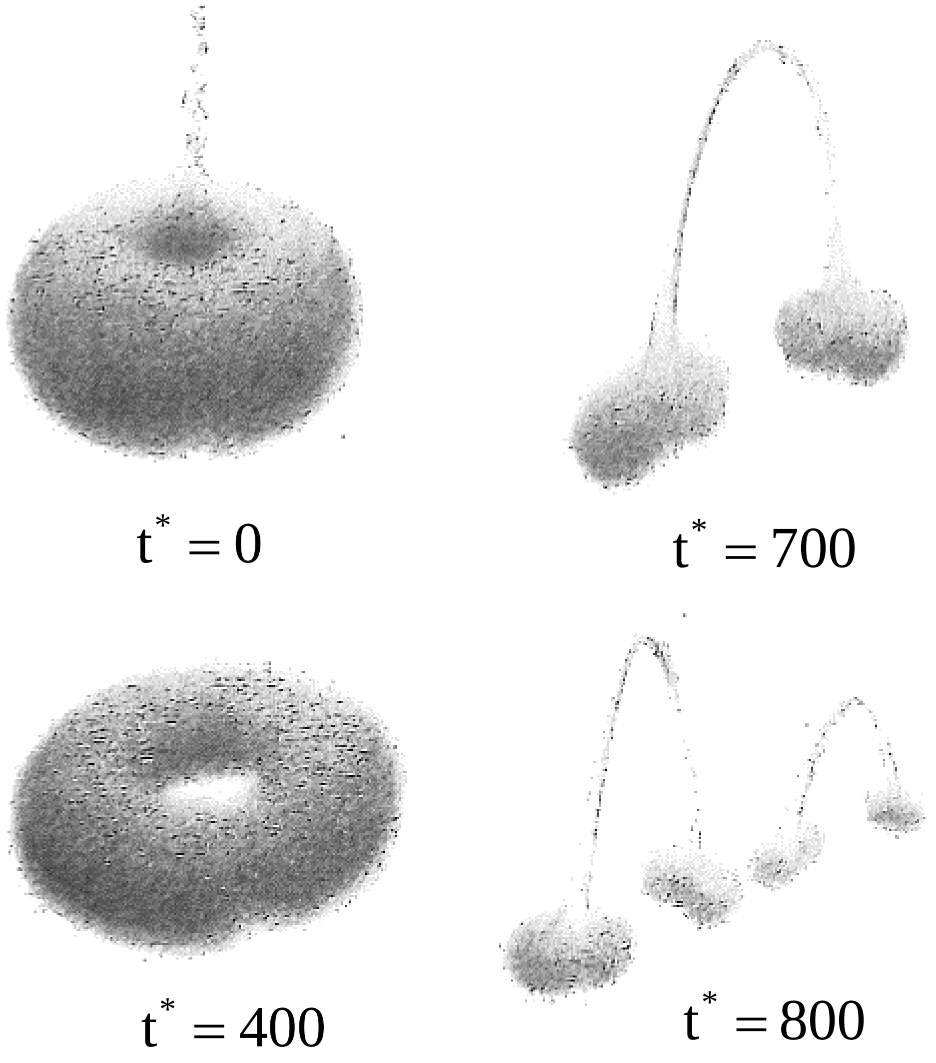


- Glass spheres (a $\approx$ 70 μm)
  (in silicon oil)

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

- 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)

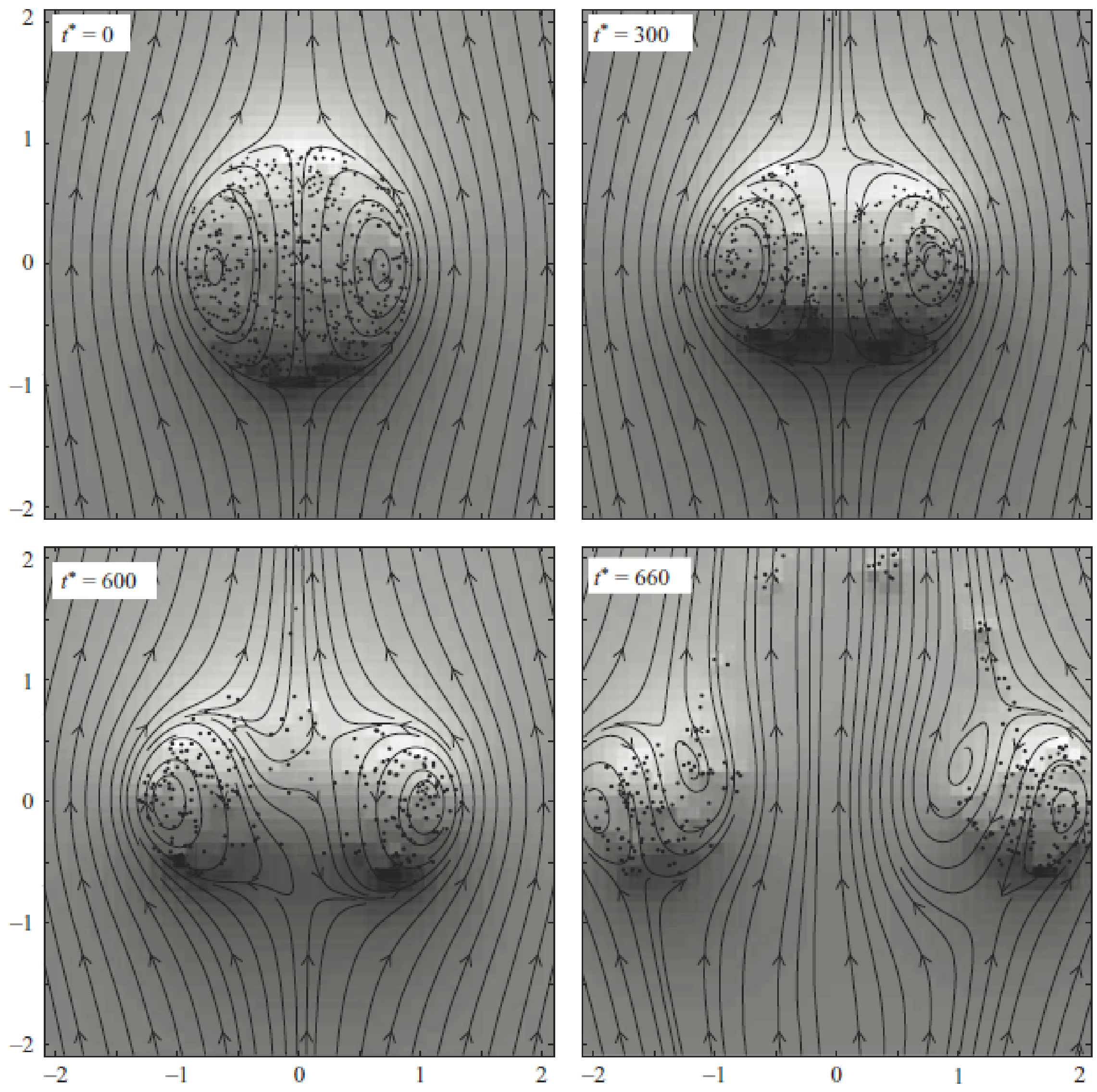
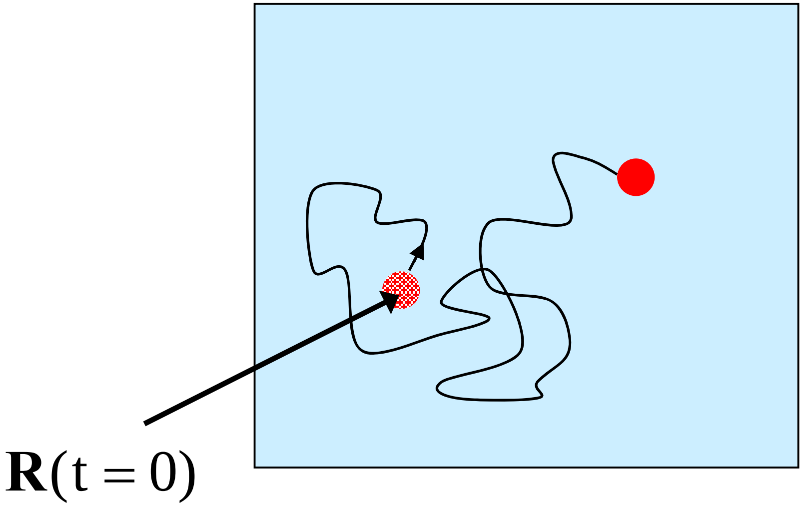


FIGURE 12. Flow and pressure fields computed at successive times in the vertical plane through the vertical axis of symmetry and in the instantaneous reference frame of the cloud. The displayed particles are those located at $\pm 0.1 R_0$ from the vertical plane. High (low) pressure is indicated in dark (white).

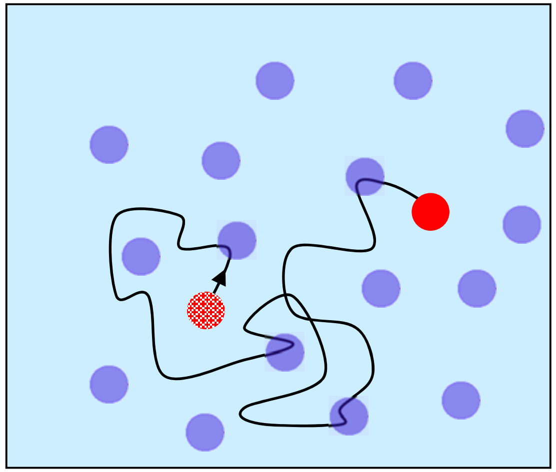
taken from: B. Metzger, M. Nicolas and E. Guazzelli, J. Fluid Mech. **580,** 238 (2007)

2.2 Macroscopic transport properties

Self - diffusion of colloids (Brownian particles)



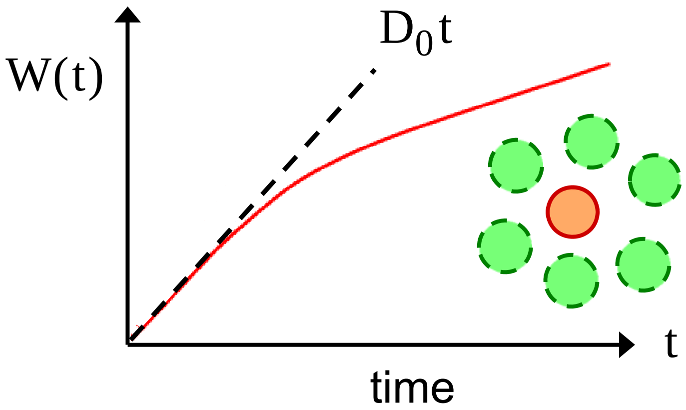
Single - sphere diffusion

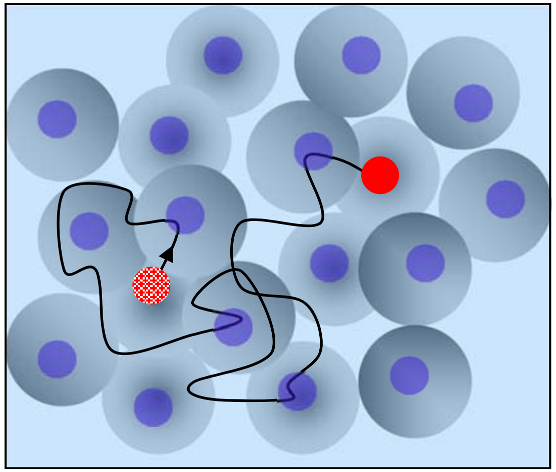


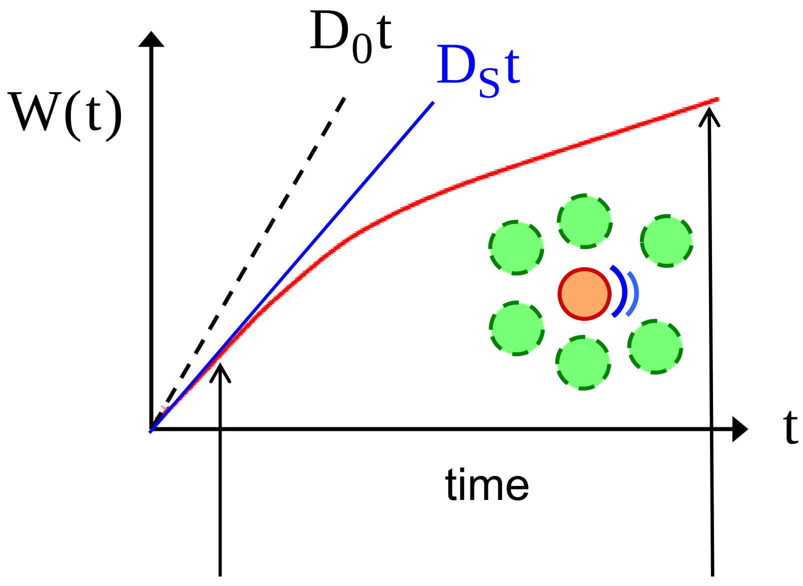
direct interactions only

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

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



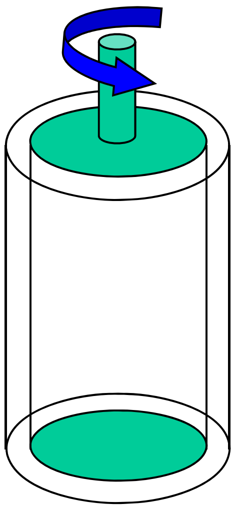




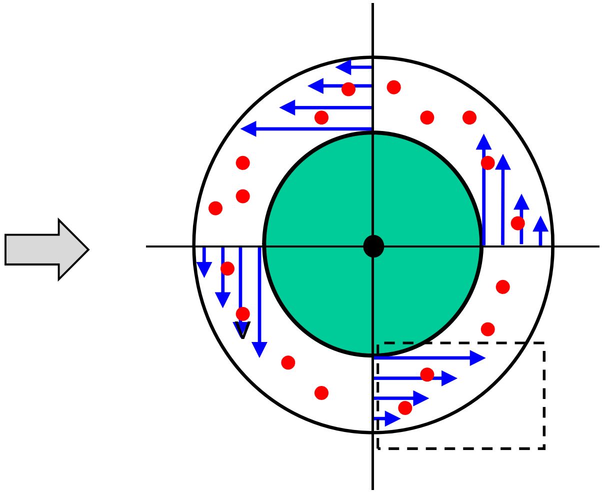
$$D_S = \frac{k_B T}{3} \mathrm{Tr} \left\langle \boldsymbol{\mu}_{11}^{tt} \right\rangle_{eq}$$

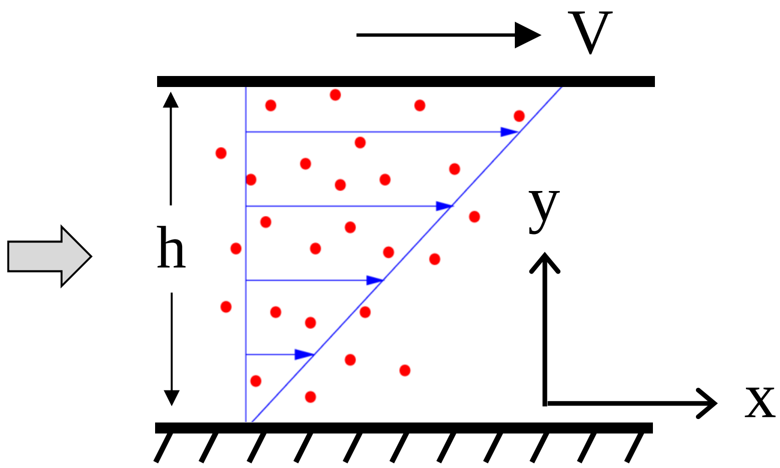
- Self – diffusion in general slowed down by hydrodynamic forces

Macroscopic shear viscosity of colloidal dispersions (Brownian)



rotational
viscosimeter





$$\mathbf{u}(y) = \dot{\gamma}\, y\, \hat{\mathbf{x}}$$

$$\frac{F_x}{\text{Area}} = \eta \frac{du_x}{dy}$$

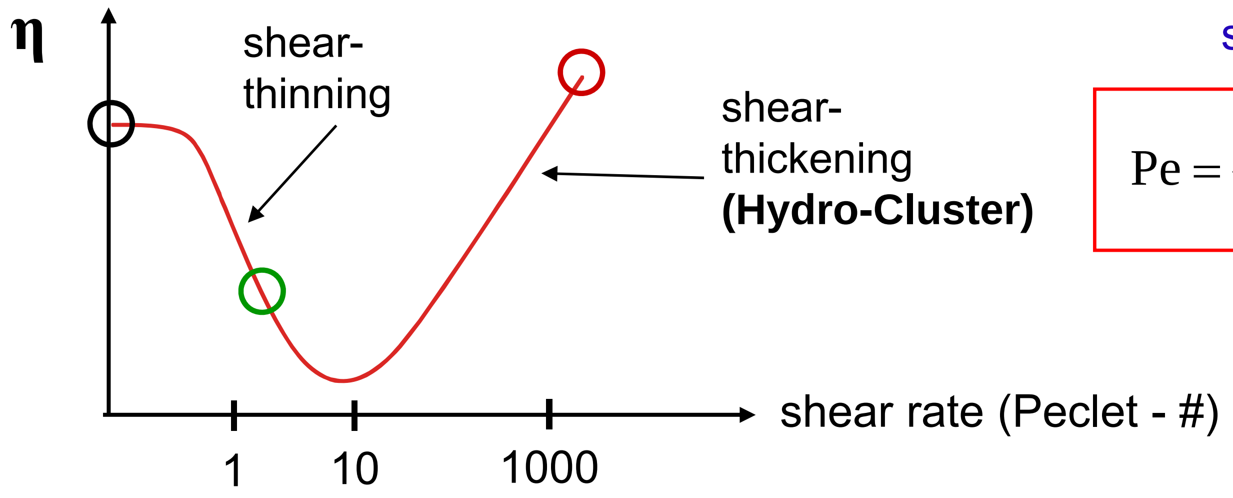
$$\dot{\gamma} = \frac{du_x}{dy} = \frac{V}{h}$$

shear stress

viscosity
(zero frequency)

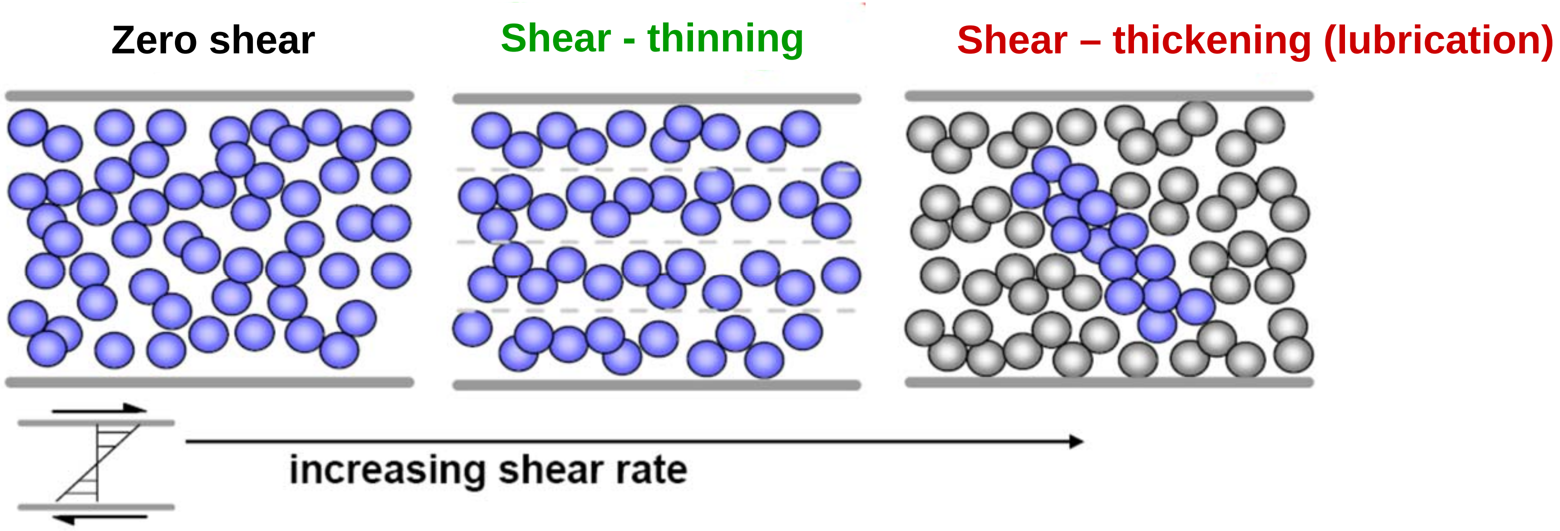
shear rate
(rate of strain)

Non – Newtonian behavior of suspension viscosity



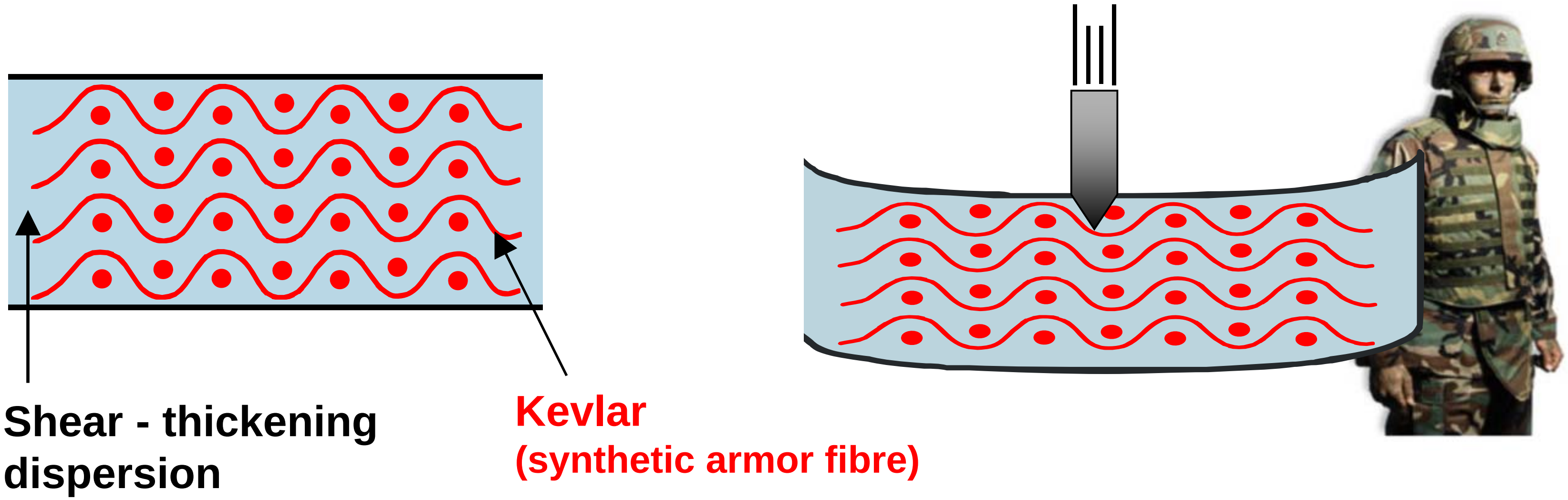
shear-Peclet #

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

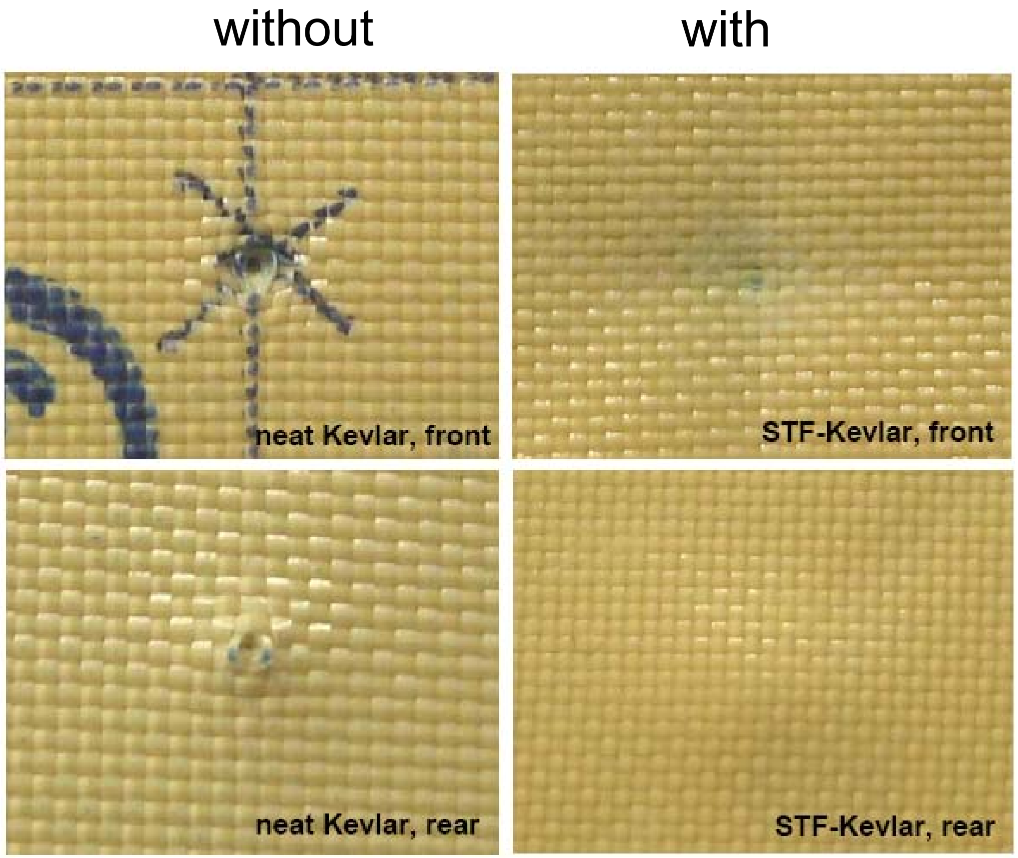


Wagner & Brady, Physics Today, October 2009

Colloidal shear-thickening: Protection against thrustings and fire arms



“Ice spike test” with and without colloid impregnation

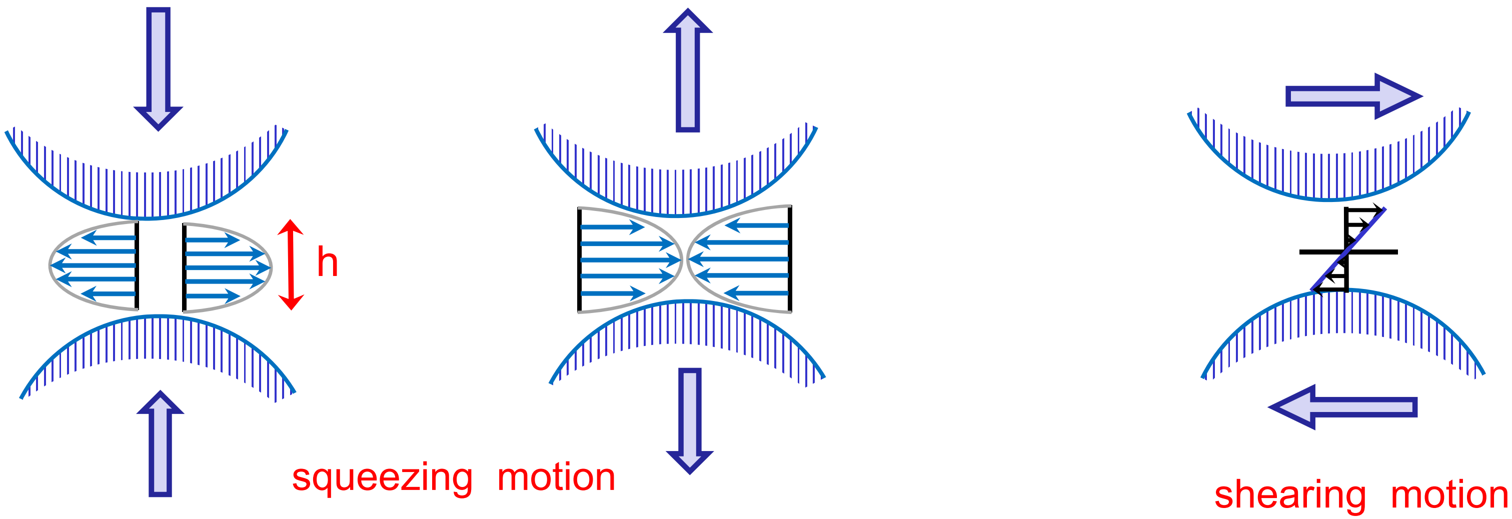


Silica in polyethylene glycol ($\phi \approx 0.52$)

Courtesy: N.J. Wagner, Univ. of Delaware, Newark

Lubrication (stick BC)

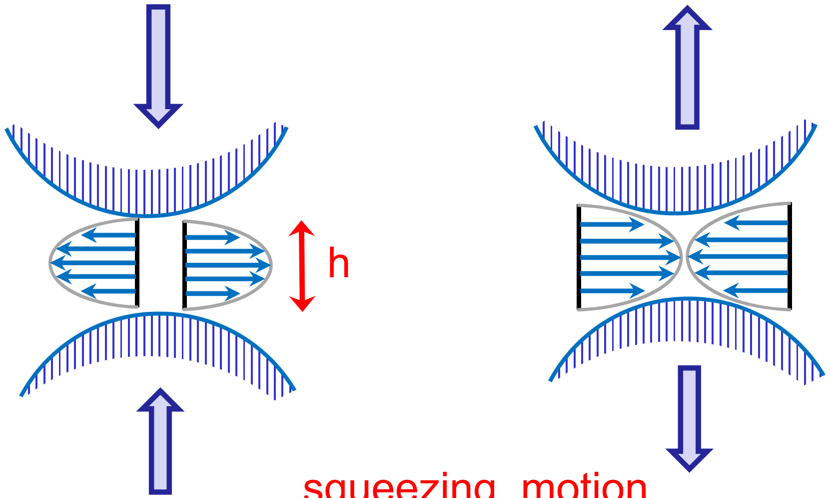
- **Dominating pressure effect in thin fluid layer between near-contact smooth surfaces**



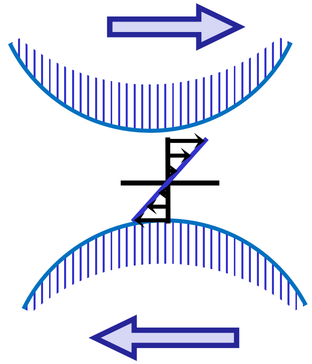
$$V_{rel} = \frac{dh}{dt} \approx -4\mu_0^t \left(\frac{h}{a}\right) F^e \qquad h = (r - 2a) \leq 0.05 \times a$$

$$h(t) \approx h(0)\, e^{-4(\mu_0/a)\, F^e\, t}$$ exponentially slow approach until roughness matters

- Finite contact time due to vdW attraction: $u(r) \approx -A_H/(r - 2a)$
- Surface roughness matters at very small distances



squeezing motion



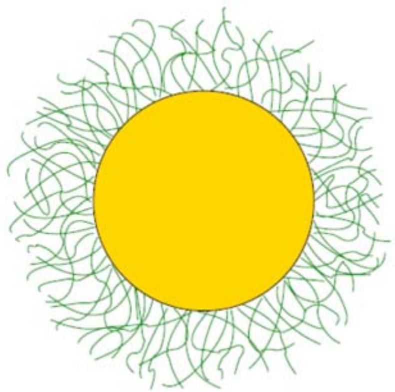
shearing motion

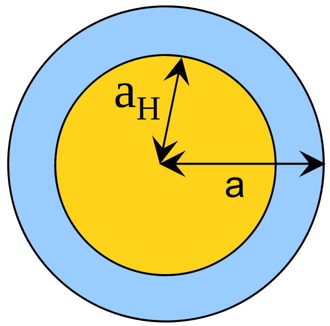
	squeezing motion	shearing motion
No-slip:	$F^e \sim \frac{a}{h} V_{rel}$	$F^e \sim \ln\left(\frac{a}{h}\right) V_{rel}$
Drop:	$F^e \sim \left(\frac{a}{h}\right)^{1/2} V_{rel}$	slip past each other
Bubble:	$F^e \sim \ln\left(\frac{a}{h}\right) V_{rel}$	slip past each other

Hydrodynamic and direct interaction radii

- Influence of stabilizing layers and porosity effects can suppress lubrication

core -shell



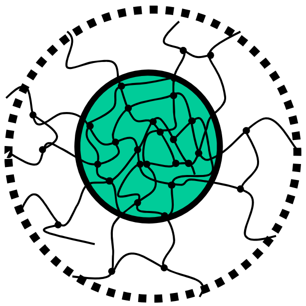


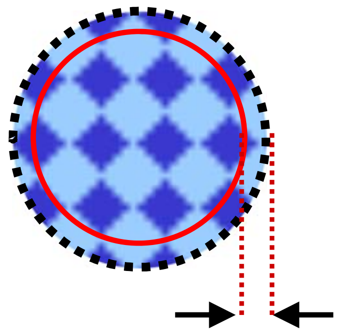
Spherical annulus model

$$a_H < a$$

$$\zeta_0^t = 6\pi\eta_0 a_H$$

microgel





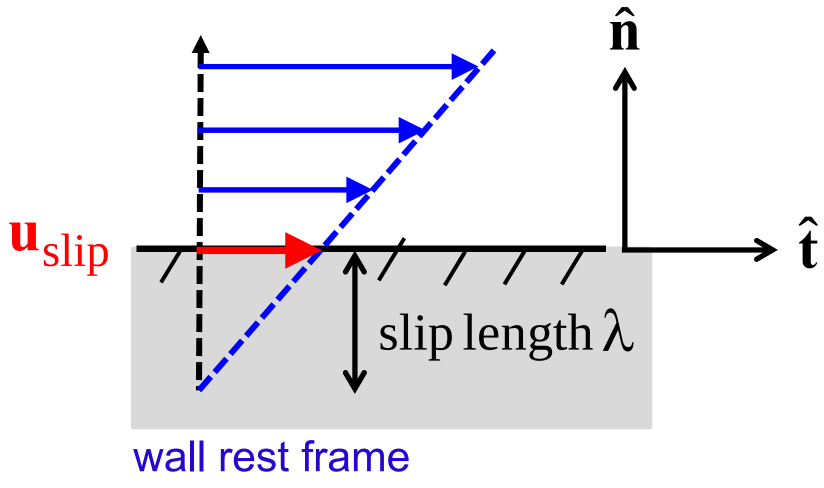
Porous hard-sphere model

λ slip length

▶ Non - zero relative squeezing mobility at contact

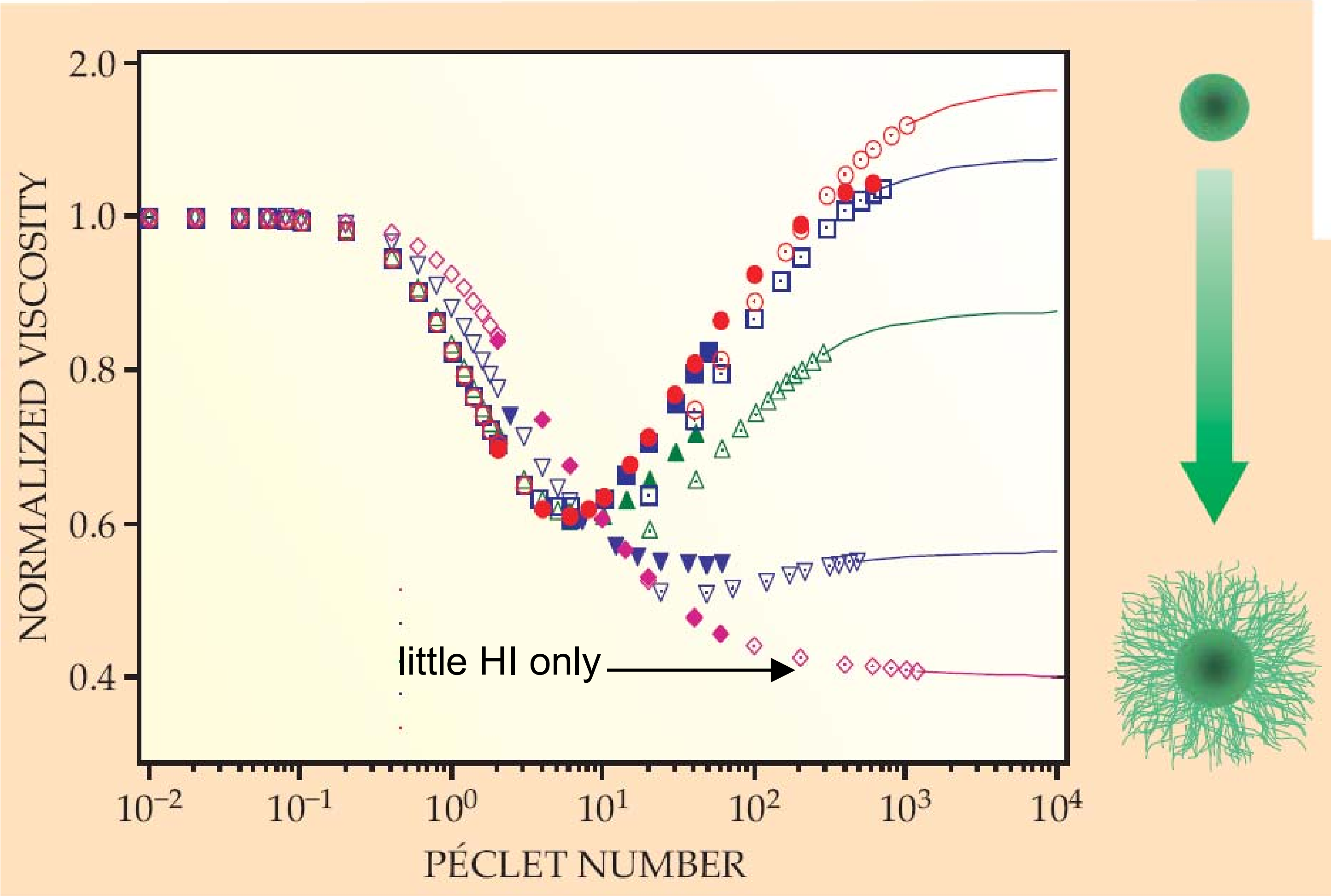
$$u_{slip} = \lambda\, \hat{\mathbf{t}} \cdot \nabla \mathbf{u} \cdot \hat{\mathbf{n}}$$

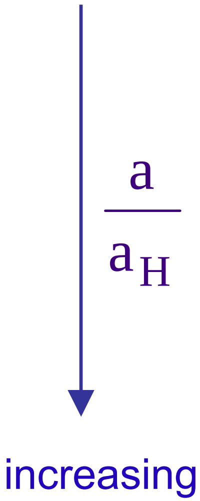
$\partial_\alpha u_\beta$



- Slip length λ: distance inside surface at which fluid velocity extrapolates to zero
- Hydrophilic surfaces
  Electric double layer
  hydration shell (ion, protein)

- **Shear thickening ceases with increasing brush thickness**





Wagner & Brady, Physics Today, October 2009

Bergenholtz, Brady & Vivic, J. Fluid Mech. **456** (2002)

3. Low-Reynolds number flow

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

Gerhard Nägele

Enrico Fermi Summer School „Physics of Complex Systems“, Varenna, Italy, July 4 – 9, 2012

3.1 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

$$\nabla\cdot\mathbf{u}(\mathbf{r},t) = 0 \qquad \Delta t \gg \tau_{sound} = a / c_{sound} \sim 10^{-10}\ \text{sec}$$

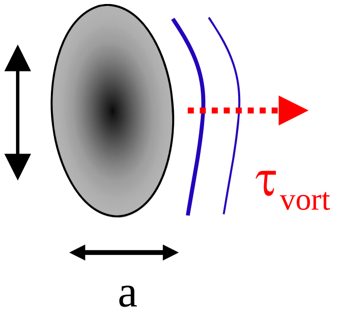
volumetric force density **on** fluid by external fields

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

(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



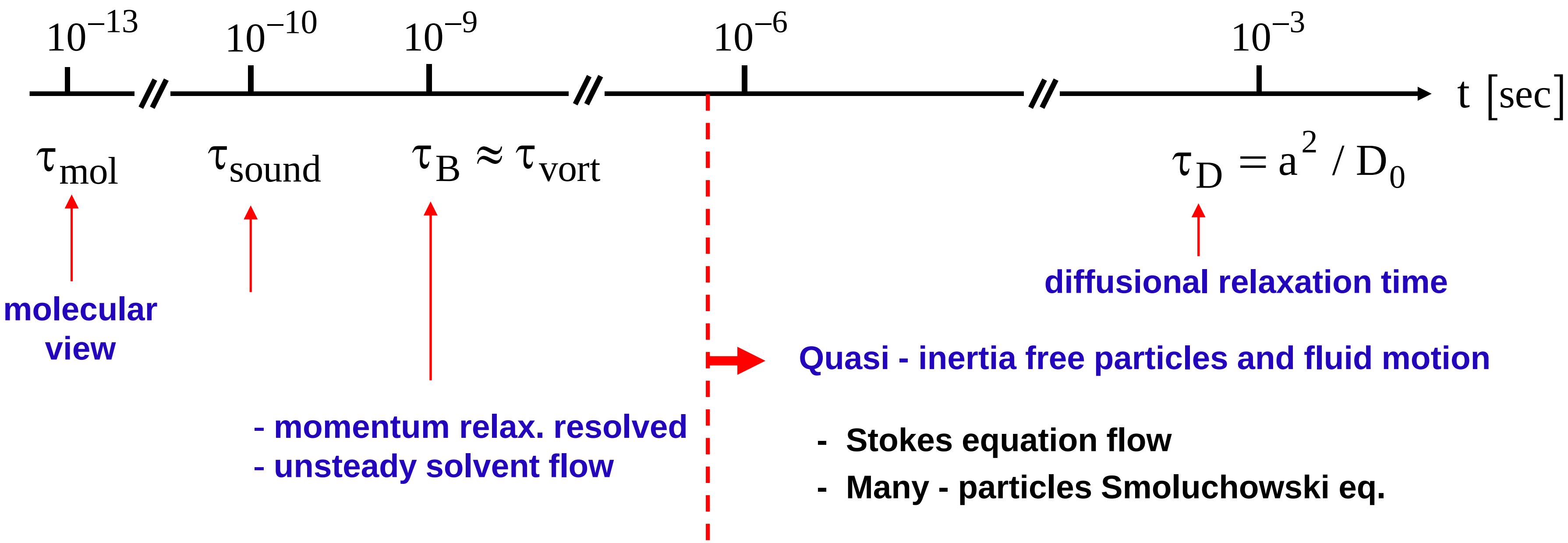
$$\Delta t \gg \tau_{vort} = \frac{a^2 \rho_f}{\eta_0} \sim 10^{-9}\ \text{sec} \quad \Longrightarrow \quad \frac{\rho_f V_p / \Delta t}{\eta_0 V_p / a^2} \ll 1$$

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

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

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

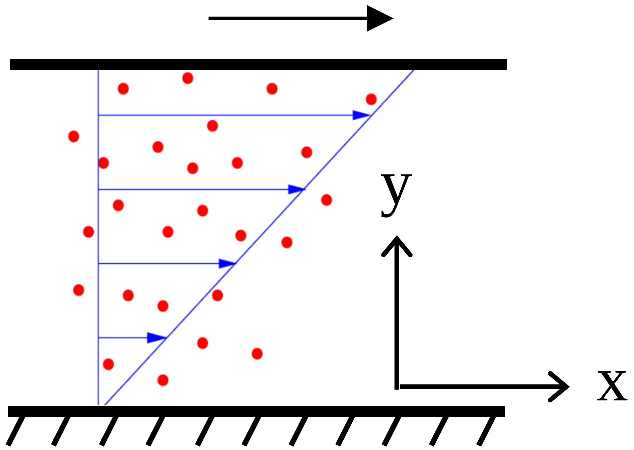
- **Colloids and microswimmer:** Re <<1 and St << 1
- Dry powder granular dynamics: St >>1 (large & heavy particles in a gas)

Shear-Peclet #

$$\mathrm{Pe} = \frac{\tau_D}{\tau_{shear}} = \dot{\gamma}\,\tau_D \propto \dot{\gamma}\,a^3$$

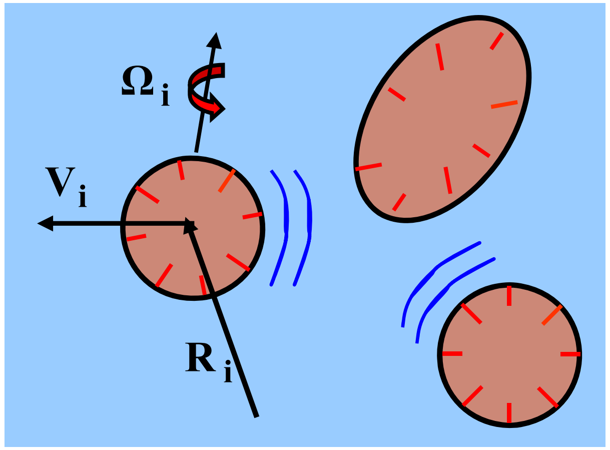
$$\tau_D = \begin{cases} 5 \text{ ms} & \text{for } a = 0.1\ \mu\text{m} \\ 5 \text{ sec} & \text{for } a = 1.0\ \mu\text{m} \\ 2 \text{ min} & \text{for } a = 5.0\ \mu\text{m} \end{cases}$$

- Pe << 1: Brownian motion is dominating
- Pe >> 1: Flow advection dominates



3.2 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)

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

Helmholtz (1868) :

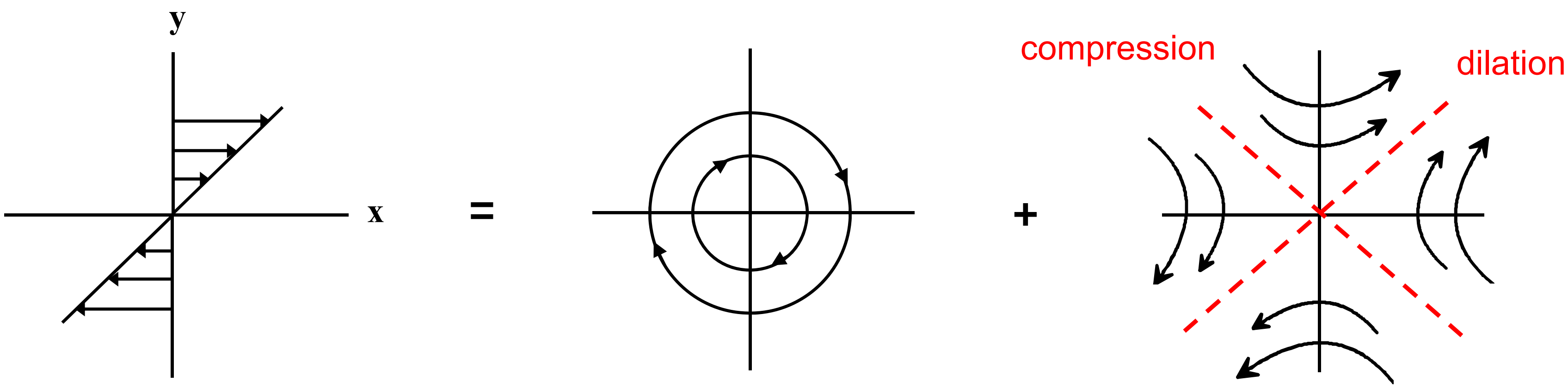
- Unique solution **u**(**r**) for given BC‘s on inner and outer fluid boundaries (see **Appendix**)
- Of all **u**(**r**) with div **u**(**r**) = 0, Stokes flow has minimal dissipation

Important ambient flow: simple linear shear flow → Rheology

$$\mathbf{u}_\infty(\mathbf{r}) = \dot{\gamma}\, y\, \hat{\mathbf{x}} = \boldsymbol{\omega}_\infty \times \mathbf{r} + \mathbf{e}_\infty : \mathbf{r}$$

$$\boldsymbol{\omega}_\infty(\mathbf{r}) = \frac{1}{2}\nabla \times \mathbf{u}_\infty(\mathbf{r}) = -\frac{1}{2}\dot{\gamma}\,\hat{\mathbf{z}}$$

$$\mathbf{e}_\infty(\mathbf{r}) = \frac{1}{2}\left[\left(\nabla\mathbf{u}_\infty\right)(\mathbf{r}) + \left(\nabla\mathbf{u}_\infty\right)^{\mathrm{T}}(\mathbf{r})\right] - \frac{1}{3}\mathrm{Tr}\left(\nabla\mathbf{u}_\infty(\mathbf{r})\right) = \frac{1}{2}\dot{\gamma}\left[\hat{\mathbf{x}}\,\hat{\mathbf{y}} + \hat{\mathbf{y}}\,\hat{\mathbf{x}}\right]$$



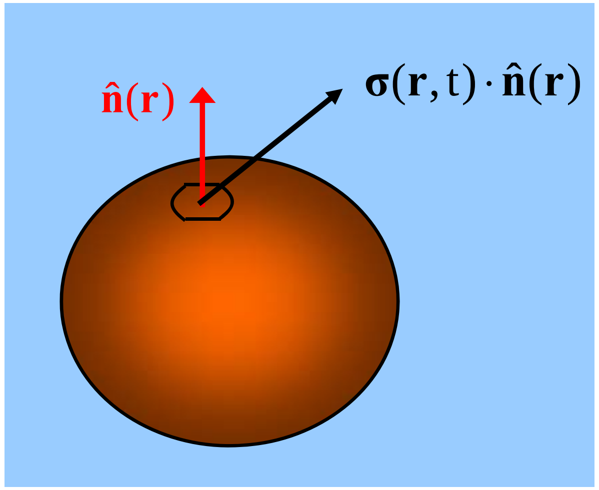
(Simple shear flow) **(Pure rotation)** **(Extensional flow)**

Stress tensor of incompressible fluid

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

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

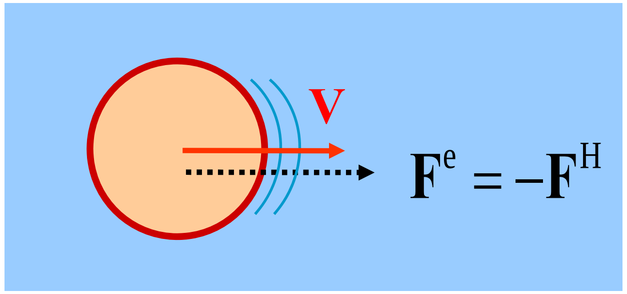
fluid stress tensor



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

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

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



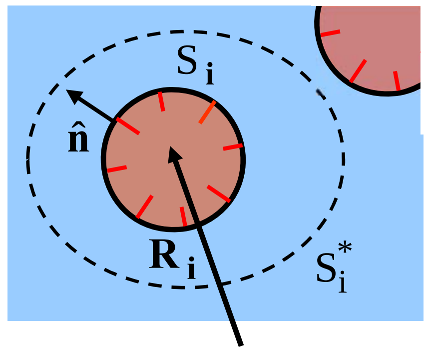
single sphere force balance

Mobility and friction matrices

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

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

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



Point - force solution (Oseen)

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

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

volumetric force density on fluid

- Solution for outer BC **u**(**r** → ∞) = 0 and p(**r** → ∞) = 0 (**Appendix**) :

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

$$\mathbf{u}(\mathbf{r}) = \mathbf{T}_0(\mathbf{r} - \mathbf{r}') \cdot \mathbf{F} \qquad \mathbf{T}_0(\mathbf{r}) = \frac{1}{8\pi\eta_0 r}\left(\mathbf{1} + \hat{\mathbf{r}}\hat{\mathbf{r}}\right)$$

Oseen tensor

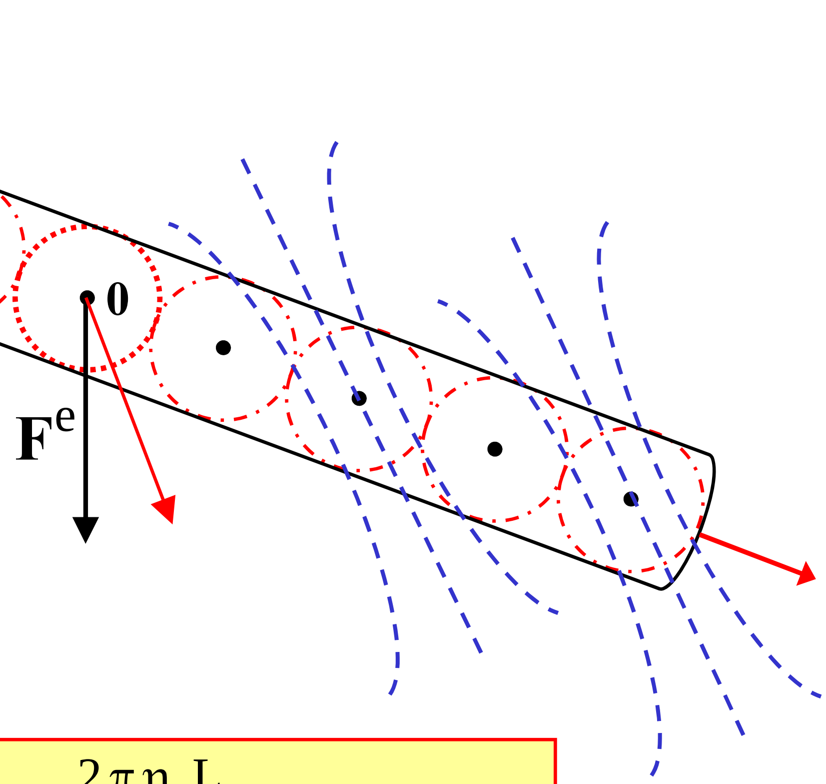
$$(\mathbf{T}_0)_{\alpha\beta}(\mathbf{r}) = \frac{1}{8\pi\eta_0 r}\left(\delta_{\alpha\beta} + \frac{x_\alpha x_\beta}{r^2}\right)$$

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

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

for localized force density acting on fluid

First application: friction coefficients of thin rod of length L and thickness d



$$\frac{L}{d} = 2n+1 \quad (n \gg 1)$$

- **Approximate by sum of Stokeslets:**

$$\mathbf{V} \approx \mathbf{u}(\mathbf{0}) = \frac{1}{\zeta_{bead}} \frac{d}{L} \mathbf{F}^e + \sum_{\substack{i=-n \\ i \neq 0}}^{n} \mathbf{T}_0(i\hat{\mathbf{e}}d) \cdot \frac{d}{L} \mathbf{F}^e$$

$$\mathbf{F}^e = \left[\zeta_{\parallel} \hat{\mathbf{e}}\hat{\mathbf{e}} + \zeta_{\perp} \left(\mathbf{1} - \hat{\mathbf{e}}\hat{\mathbf{e}} \right) \right] \cdot \mathbf{V}$$

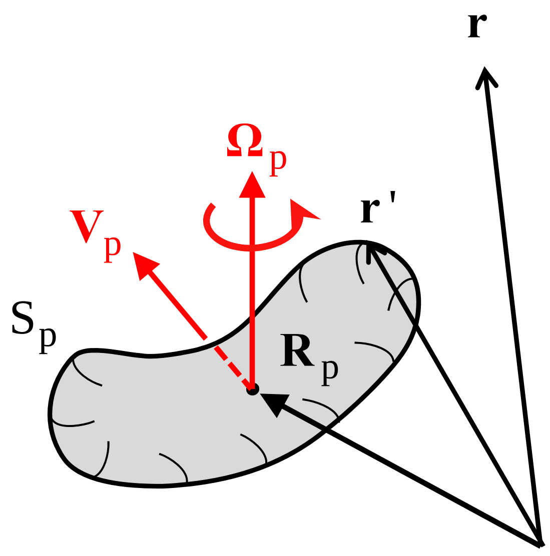
$$\zeta_{\parallel} = \frac{2\pi\eta_0 L}{\ln(L/d)} \qquad \zeta_{\perp} = 2\zeta_{\parallel}$$

- End caps correction: $\ln(L/d) \rightarrow \ln(L/d) - 0.12$

- HI of segments lowers friction and renders it anisotropic (convection - along effect)
- Friction ratio 1:2 is due to Oseen approximation: $\mathbf{1} + \hat{\mathbf{e}}\hat{\mathbf{e}} = \left(\mathbf{1} - \hat{\mathbf{e}}\hat{\mathbf{e}} \right) + 2\hat{\mathbf{e}}\hat{\mathbf{e}} = \hat{\mathbf{P}}_{\perp} + 2\hat{\mathbf{P}}_{\parallel}$

3.4 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"

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

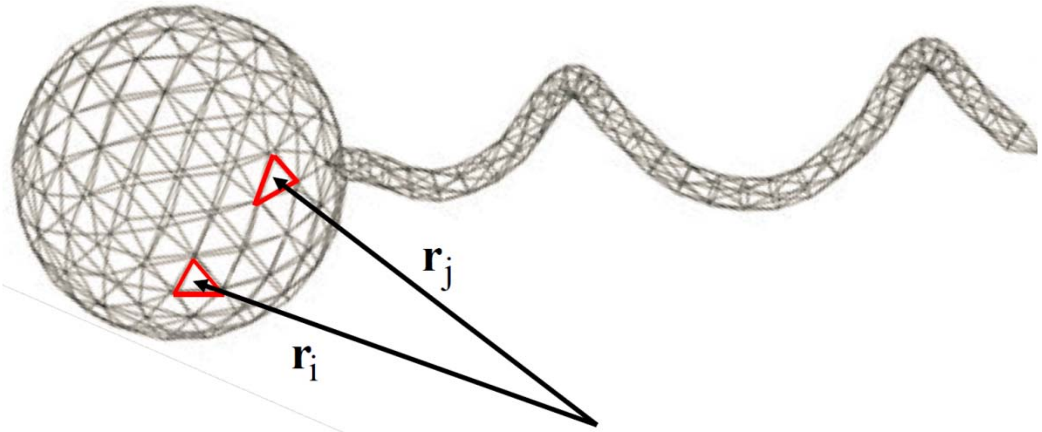
- Insertion of no - slip BC ⇨ two-dimensional integral equation for traction:

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

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

- Particle with complex shape: Discretization / Triangularization

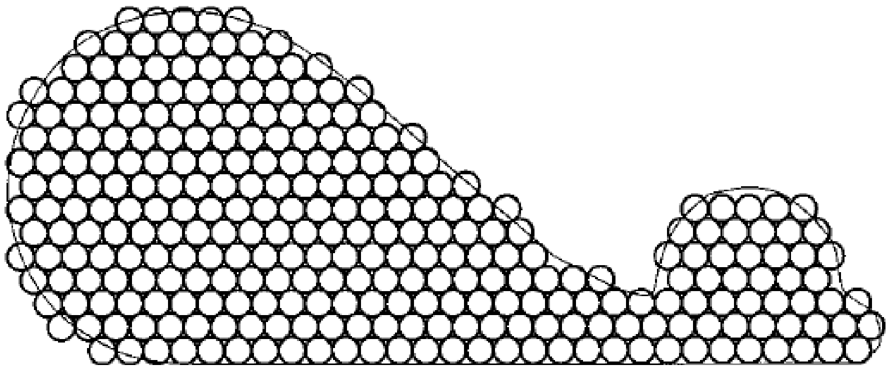
$$\mathbf{V}_p + \boldsymbol{\Omega}_p \times (\mathbf{r}_i - \mathbf{R}_p) - \mathbf{u}_\infty(\mathbf{r}_i) = \sum_{j=1}^{N} \underbrace{\mathbf{T}_0(\mathbf{r}_i - \mathbf{r}_j)}_{3N\times 3N \text{ inversion}} \cdot \mathbf{f}^{(s)}(\mathbf{r}_j) \qquad (i \in \{1, \ldots, N\})$$



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

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

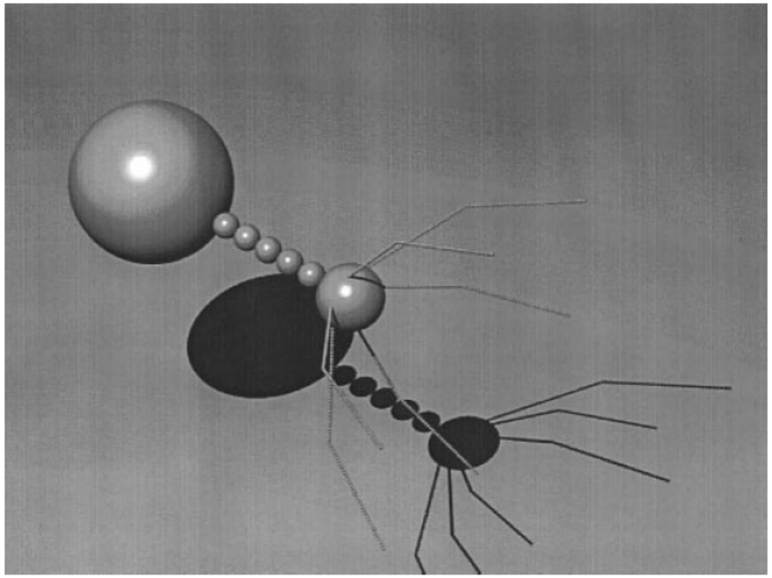
Bead modeling of complex-shaped particles



B. Carrasco & **J. Garcia de la Torre**,

Biophysical J. **75** (1999)

HYDROPRO packages



T2 – bacteriophage model

(V. Bloomfield, Biopolymers 5 (1967))

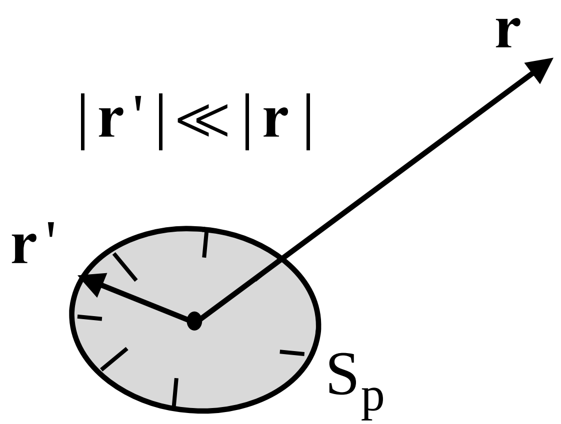
- Preserve original volume
- Rotne-Prager-Yamakawa HI approximation!

– Intrinisic viscosity

– Mobilities & friction coefficients etc.

Far – distance flow field around a 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

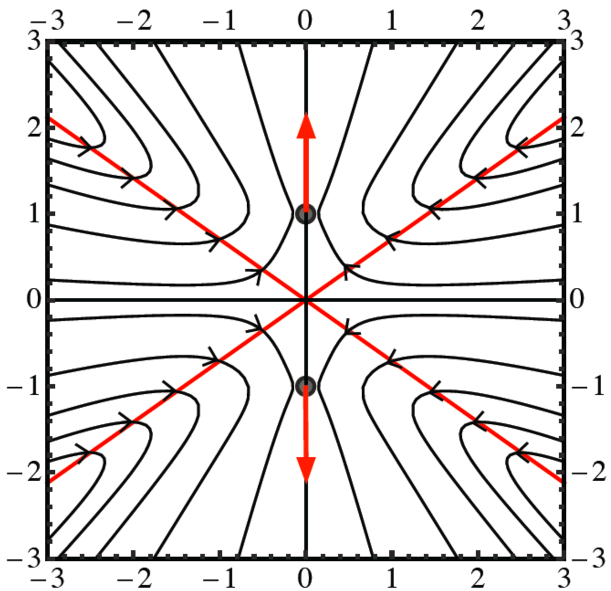
Example: symmetric force dipole in y - direction (pusher: p > 0)

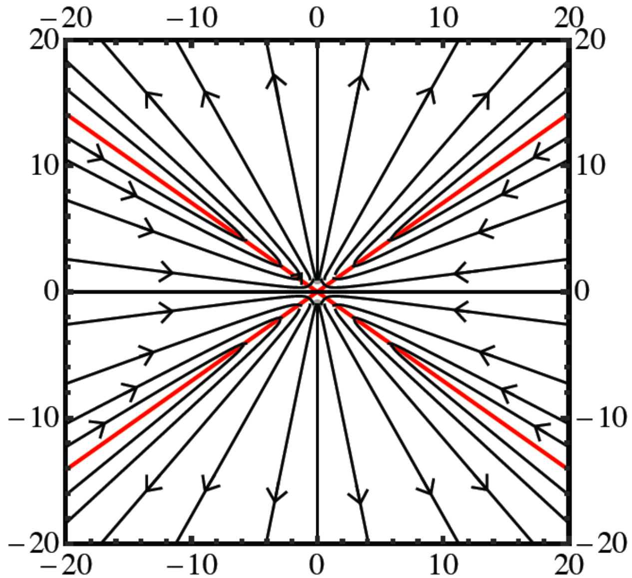
$$\mathbf{u}(\mathbf{r}) = \left[\mathbf{T}_0(\mathbf{r} - \frac{d}{2}\hat{\mathbf{y}}) - \mathbf{T}_0(\mathbf{r} + \frac{d}{2}\hat{\mathbf{y}})\right] \cdot F^e\,\hat{\mathbf{y}}$$

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

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

dipole moment



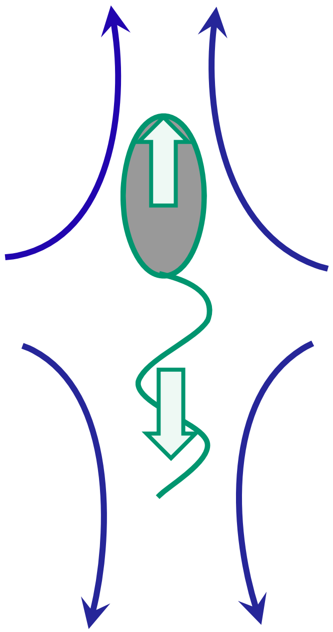


- Far – field flow : $\cos\theta = \hat{\mathbf{y}} \cdot \hat{\mathbf{r}}$

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

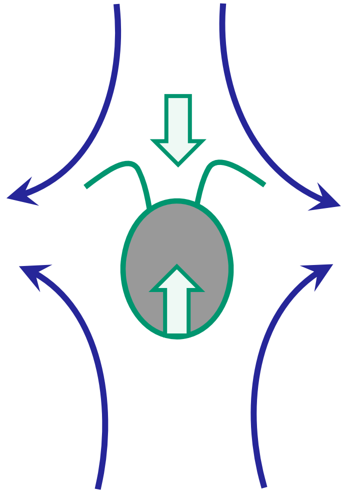
- Swimmer describeable as static force dipole for distances >> d , and when time – averaged over strokes (non-reciprocal cycle, friction-asymmetric)

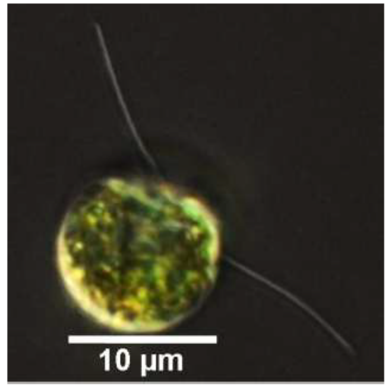
- **Pusher: p > 0**



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

- **Puller: p < 0**





Production stroke

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

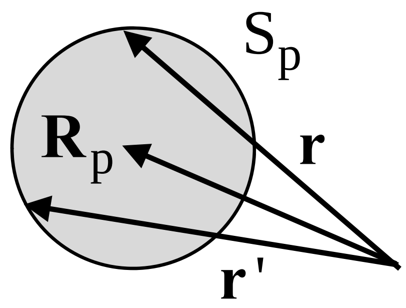
Faxén laws for spheres

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

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

$$\Rightarrow \Delta p_\infty(\mathbf{r}) = 0 \quad \Rightarrow \quad \boxed{\Delta \Delta \mathbf{u}_\infty(\mathbf{r}) = 0}$$ (**bi - harmonic** $\longrightarrow$ mean - value property: **Appendix**)

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



- 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

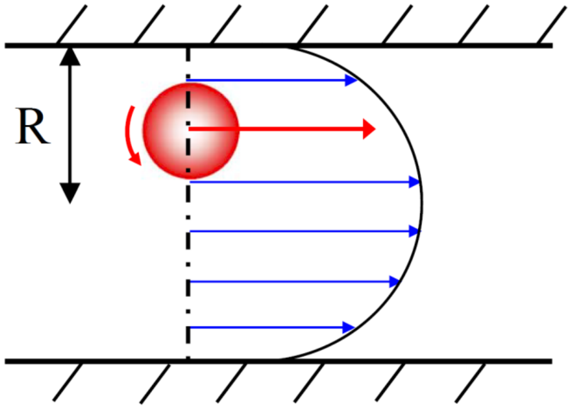
$$\mathbf{F}_p^H = -6\pi\eta_0 a\left[\mathbf{V}_p - \left(\mathbf{1} + \frac{a^2}{6}\nabla^2\right)\mathbf{u}_\infty(\mathbf{r} = \mathbf{R}_p)\right]$$

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

extra non - linear flow contribution

- Rotational Faxén law:

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



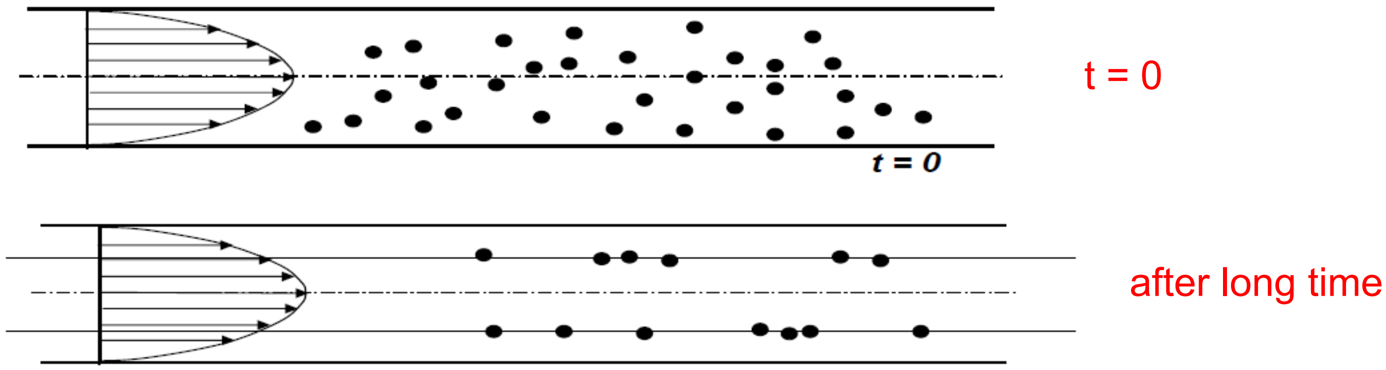
$$\mathbf{F}^H = \mathbf{0} = \mathbf{T}^H :$$

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

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

- 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

4. Active Microswimmers

- Kinematic reversibility
- Scallop theorem
- Artificial swimmers

4.1 Kinematic reversibility

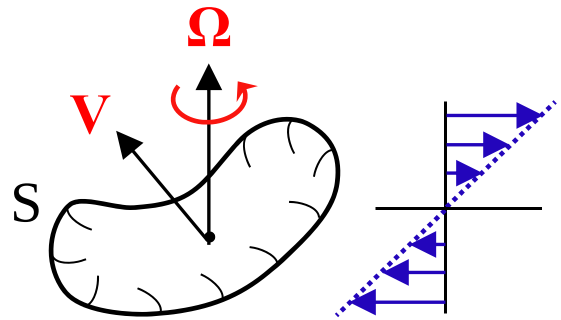
$$-\nabla p(\mathbf{r}) + \eta_0 \nabla^2 \mathbf{u}(\mathbf{r}) + \mathbf{f}_{\text{ind}}(\mathbf{r}) + \mathbf{f}^{e}(\mathbf{r}) = 0$$

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

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

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

ambient given flow
(flow w/o particles)



$$\mathbf{f}_{\text{ind}} = \mathbf{f}_{\text{ind}}(\mathbf{V}, \boldsymbol{\Omega}, [\,\mathbf{u}_\infty\,])$$

linear relation

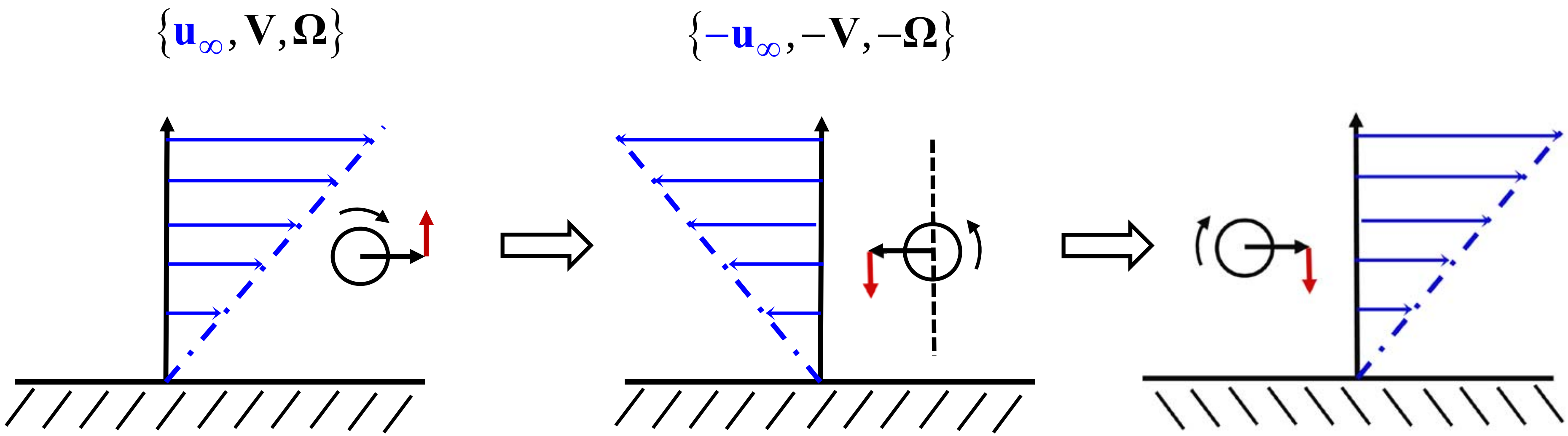
induced force density on fluid
localized on S (rigid particle)

- Since linear boundary value problem (BVP):

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

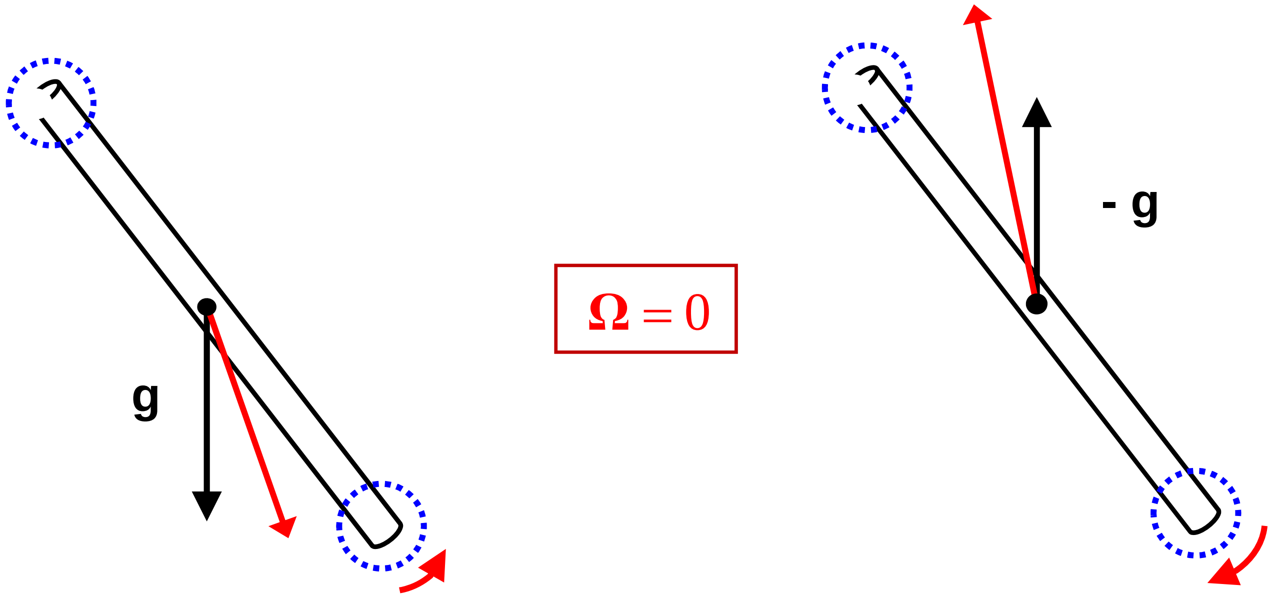
▶ Motion reversal of boundaries, external force density and ambient flow reverses sign of flow pattern only, not its shape.

Application: motion in highly symmetric systems

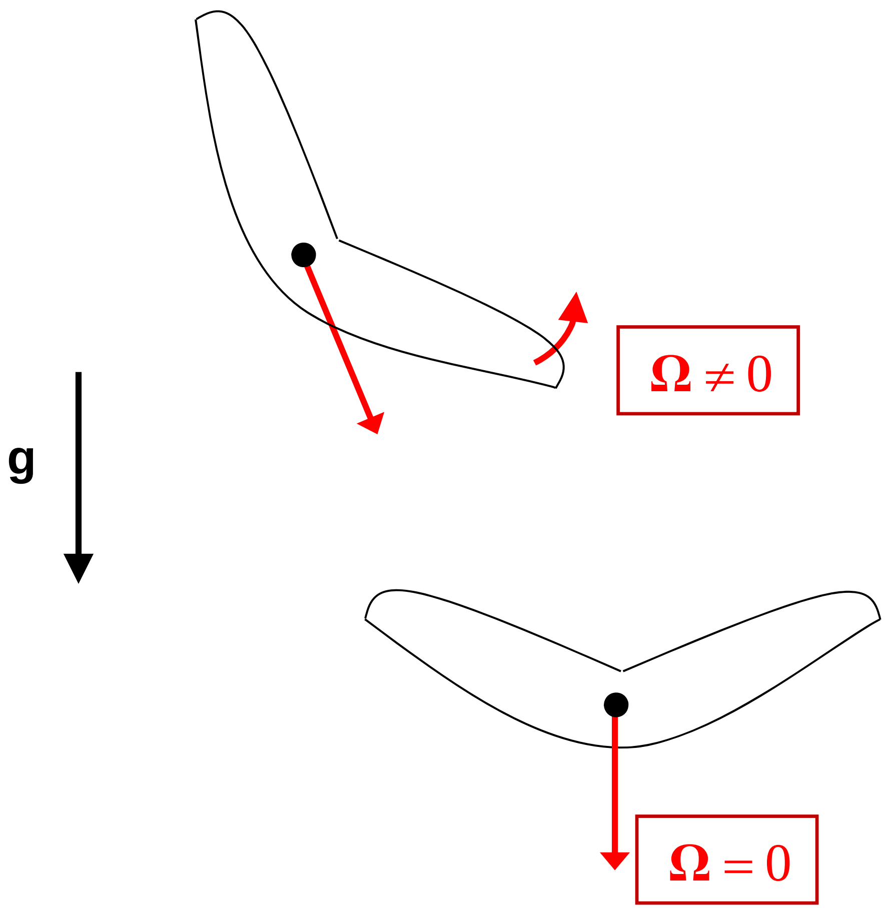


$$\Delta \mathbf{V} = 0$$

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

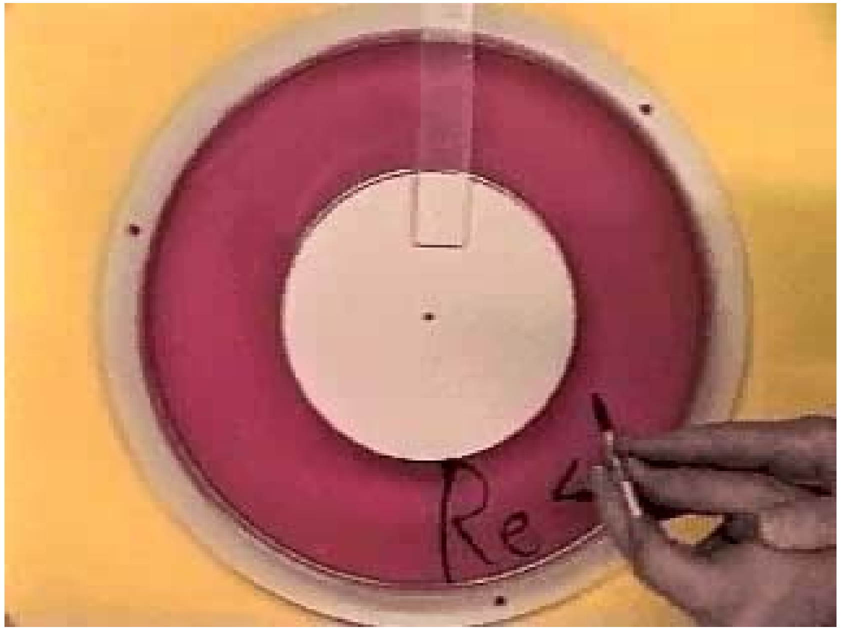


- Three symmetry planes: symmetric rod sediments sidewise w/o rotation

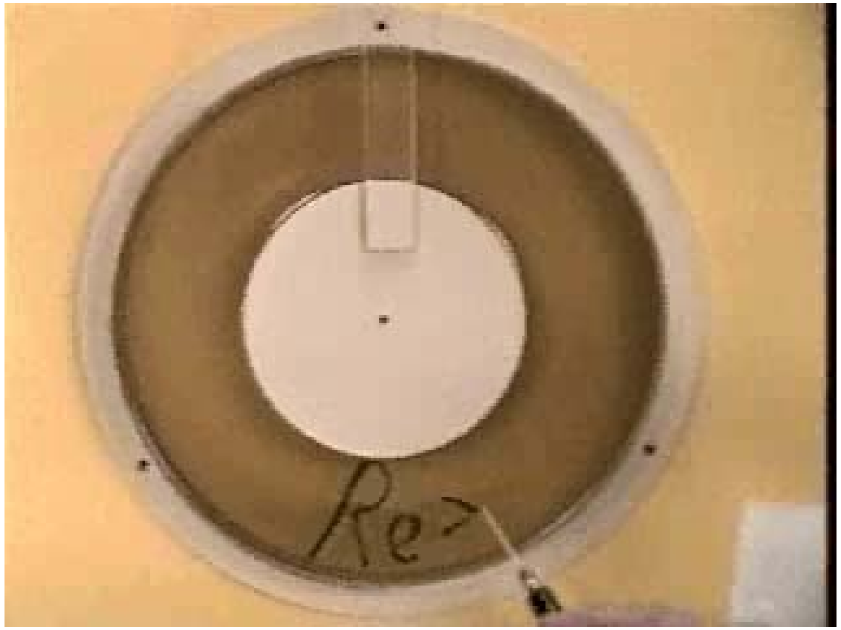


$$\begin{pmatrix} \mathbf{V} \\ \boldsymbol{\Omega} \end{pmatrix} = \underbrace{\begin{pmatrix} \boldsymbol{\mu}^{tt} & \boldsymbol{\mu}^{tr} \\ \boldsymbol{\mu}^{rt} & \boldsymbol{\mu}^{rr} \end{pmatrix}}_{\substack{\text{geometry - dep.} \\ \text{BC - dep.}}} \cdot \begin{pmatrix} \mathbf{F}^{e} = M^{*}\mathbf{g} \\ \mathbf{T}^{e} = 0 \end{pmatrix}$$

- Boomerang-shaped body rotates while sedimenting until symmetric orientation reached
- No rotation, when line of gravity through c.o.m. intersects hydrodynamic center of friction



Highly viscous fluid

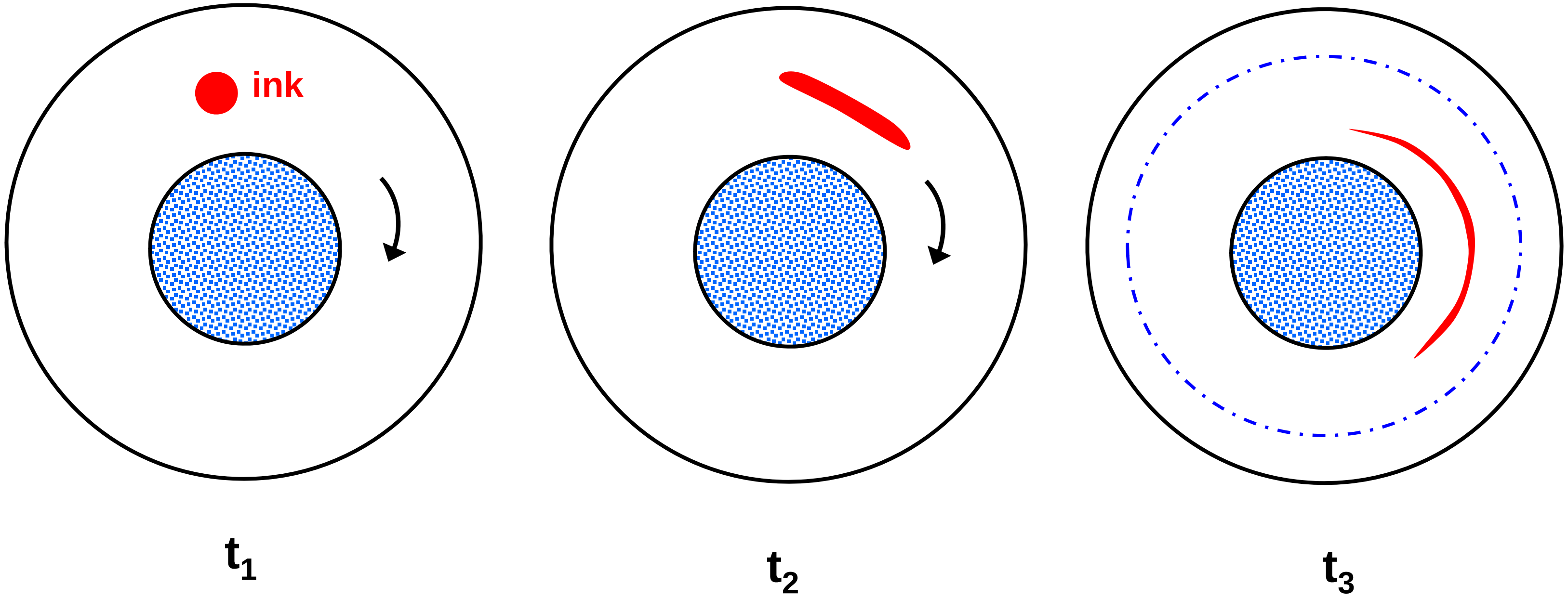


Low - viscosity fluid

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

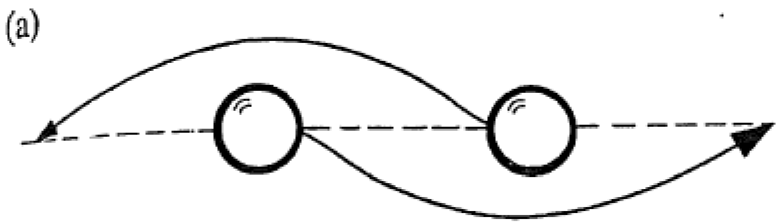
- Irreversible motion of dye across circular stream lines for Re > 1
- Diffusion causes cross-streamlines particle motion

G.I. Taylor, Cambridge

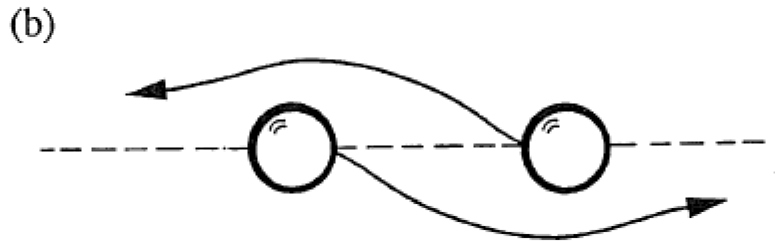


- **Particle motion across circular stream lines induced by:**
  - Brownian motion or external noise source
  - Inertia effects (Re ~ 1)
  - Many - particle HI in sufficiently dense systems (chaotic hydrodynamic motion)
  - Reversibility - breaking direct particle interactions such as surface roughness

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

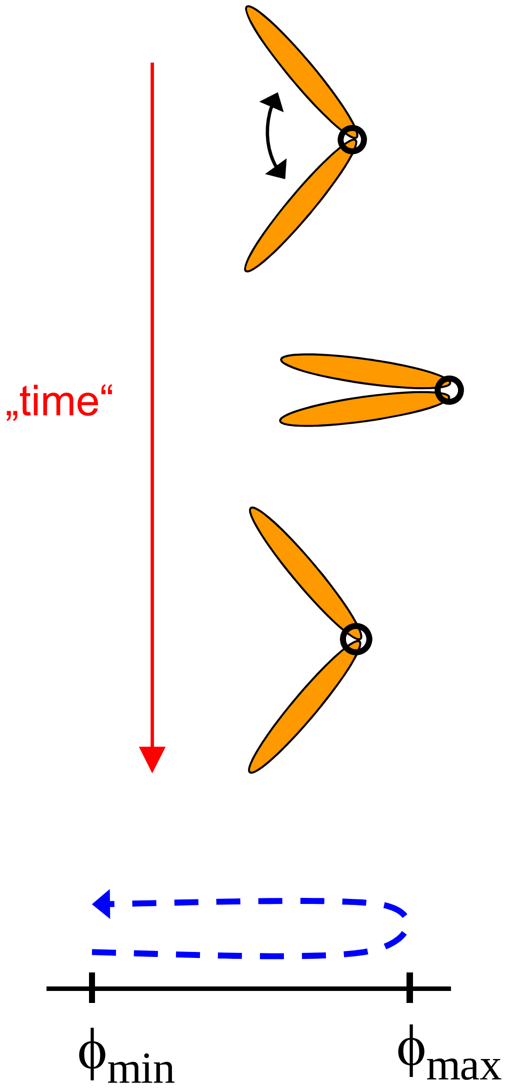


Ideal spheres, HI only



spheres with surface roughness
(lateral displacement after „collision“)

4.2 Scallop theorem



- **Internal forces and energy sources 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 for example

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

G.I. Taylor, Cambridge

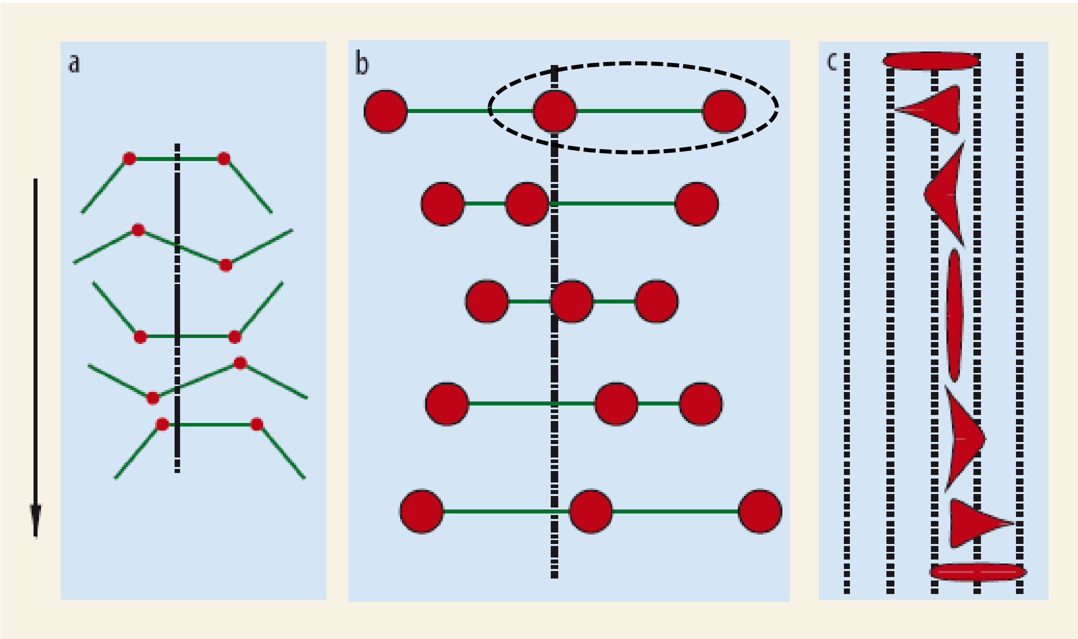
- Non-reciprocal periodic motion is required: - **helical flagellum motion**

  - **two degrees of freedom for motion**

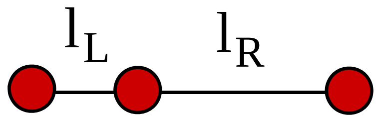
Re << 1: microrganism in water or macroscopic swimmer in glycerin

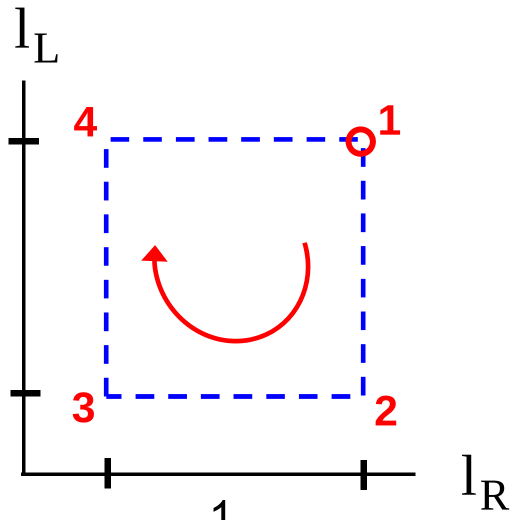
4.3 Artificial swimmers

Purcell swimmer | 3 - spheres swimmer | artificial amoeba



H. Stark, *Immer in Bewegung,* Physik Journal **6**, Nr. 10 (2007)





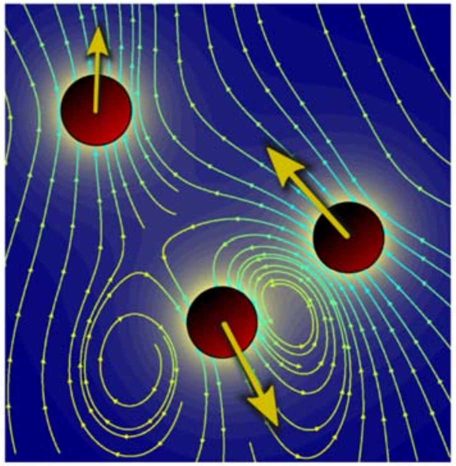
$$\delta V_L = \frac{1}{\zeta_0} \cdot F_{int}$$

$$\delta V_R = \frac{1}{\zeta_{pair}(l_R)} \left(-F_{int}\right)$$

$$\zeta_0 < \zeta_{pair}$$

5. Many- spheres HI

- General properties
- Mobility matrices



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

Gerhard Nägele

Enrico Fermi Summer School „Physics of Complex Systems“, Varenna, Italy, July 4 – 9, 2012

5.1 General properties

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

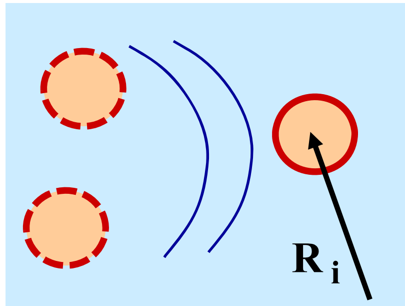
$$-\mu_0^t \mathbf{F}_i^H = \mathbf{V}_i - \left(\mathbf{1} + \frac{a^2}{6}\Delta_i\right) \sum_{k \neq i}^{N} \int_{S_j} dS' \, \mathbf{T}_0(\mathbf{r}' - \mathbf{R}_i) \cdot \mathbf{f}_k^{(s)}(\mathbf{r}')$$

Faxen 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 :**

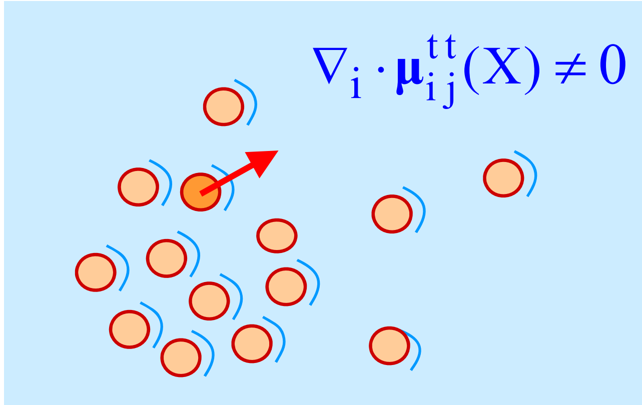
$$\mathbf{V}_i \approx -\sum_{j=1}^{N} \mu_0 \left\{\mathbf{1}\delta_{ij} + (1 - \delta_{ij})\mathbf{T}_{RP}(\mathbf{R}_i - \mathbf{R}_j)\right\} \cdot \mathbf{F}_j^H = -\sum_{j=1}^{N} \boldsymbol{\mu}_{ij}^{RP}\left(\mathbf{R}_{ij}\right) \cdot \mathbf{F}_j^H$$

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

Rotne – Prager approximation

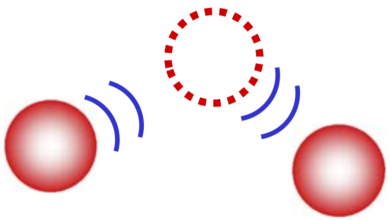
$$\begin{pmatrix} V \\ \Omega \end{pmatrix} = - \begin{pmatrix} \mu^{tt}(X) & \mu^{tr}(X) \\ \mu^{rt}(X) & \mu^{rr}(X) \end{pmatrix} \cdot \begin{pmatrix} F^H \\ T^H = 0 \end{pmatrix}$$

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



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)

⊖ All flow reflections neglected

⊖ Overestimates HI in general

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

Appendix: Multipole method by Cichocki and coworkers

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 :

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

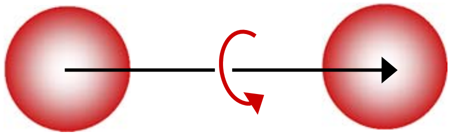
$$\boldsymbol{\omega}_{11}(\mathbf{r}) = \underbrace{-\frac{15}{4}\left(\frac{a}{r}\right)^4}_{\text{first self reflection}} \hat{\mathbf{r}}\hat{\mathbf{r}} + O\left(r^{-6}\right)$$

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

Two - spheres translational mobilities in infinite fluid

- axial symmetry and isotropy

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



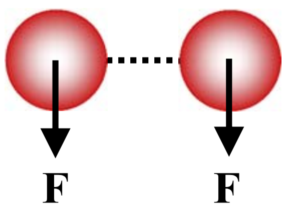
$$\mathbf{r} = \mathbf{R}_2 - \mathbf{R}_1$$

$$\boldsymbol{\omega}_{12} = \boldsymbol{\omega}_{21}$$

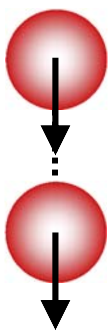
$$\boldsymbol{\omega}_{11} = \boldsymbol{\omega}_{22}$$

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

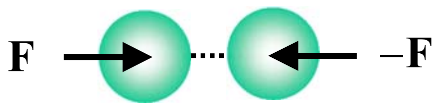
- known recursion relations for (a / r) expansion & lubrication corrections



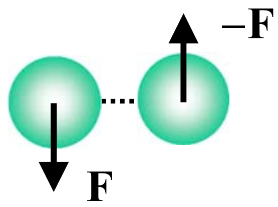
$$\mathbf{V}_i = \mathbf{V}_{sed} = (y_{11} + y_{12})\mu_0 \mathbf{F}$$



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



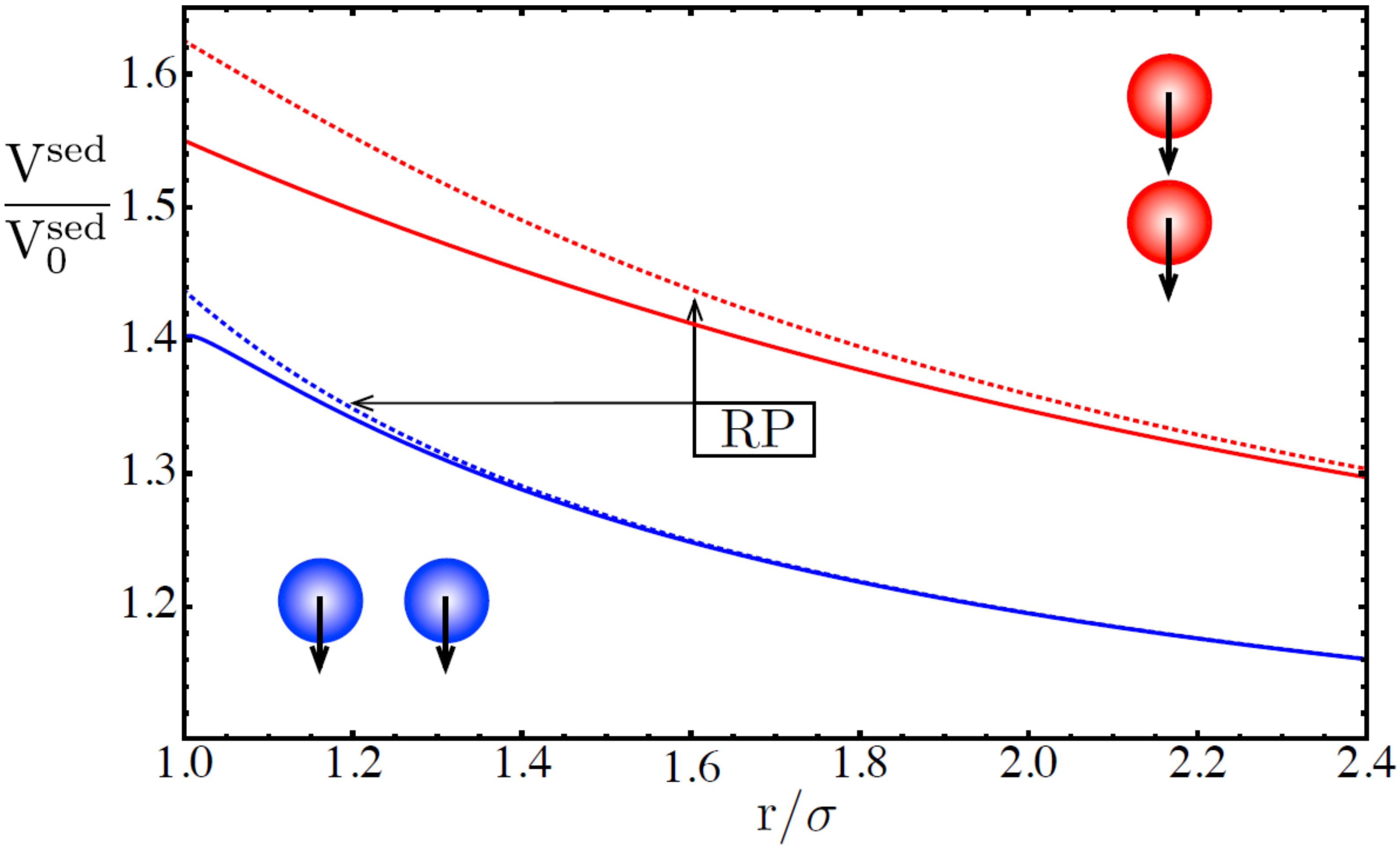
$$\Delta\mathbf{V}_{12} = 2(x_{11} - x_{12})\mu_0 \mathbf{F}$$



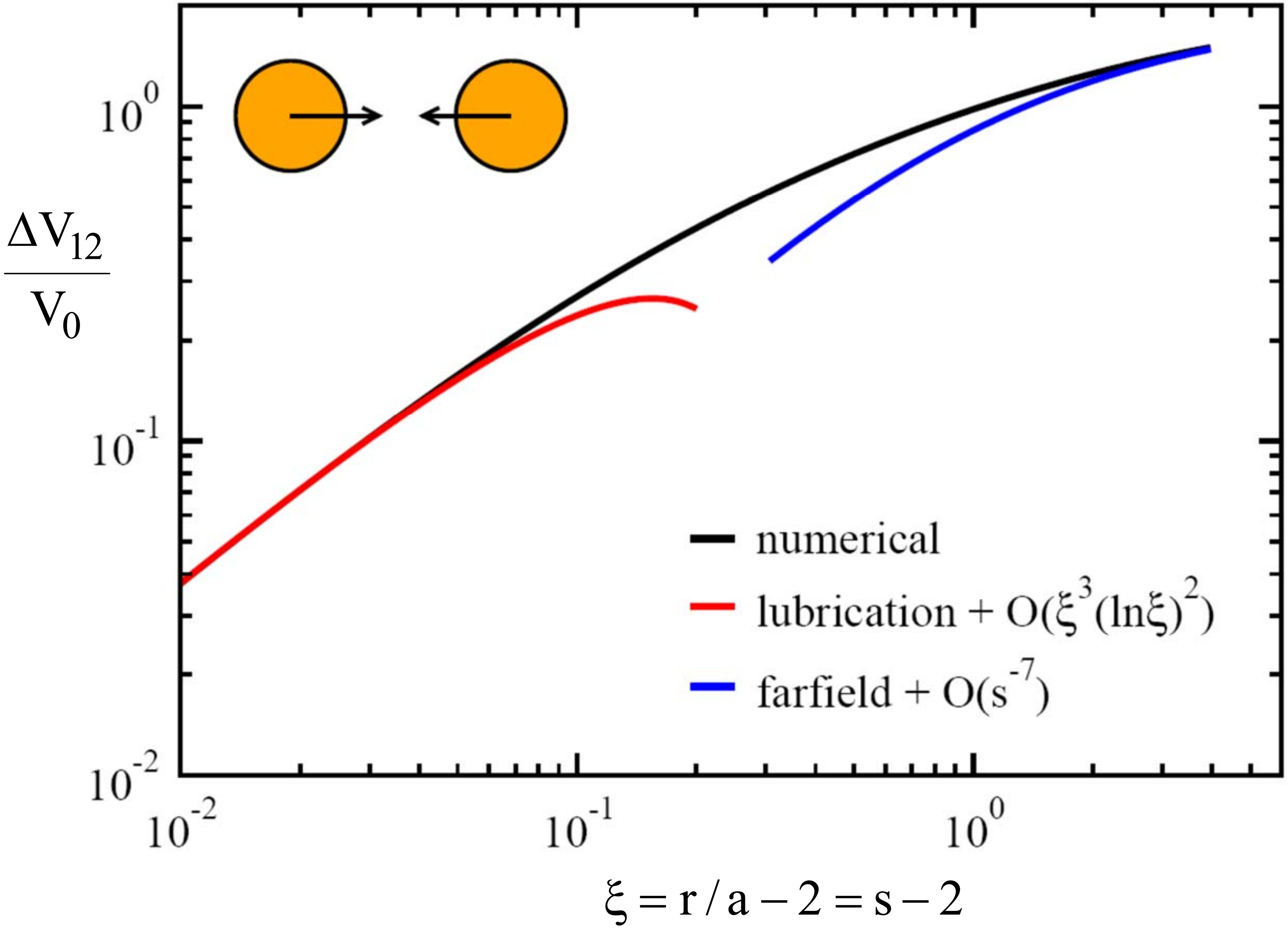
$$\Delta\mathbf{V}_{12} = 2(y_{11} - y_{12})\mu_0 \mathbf{F}$$

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

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

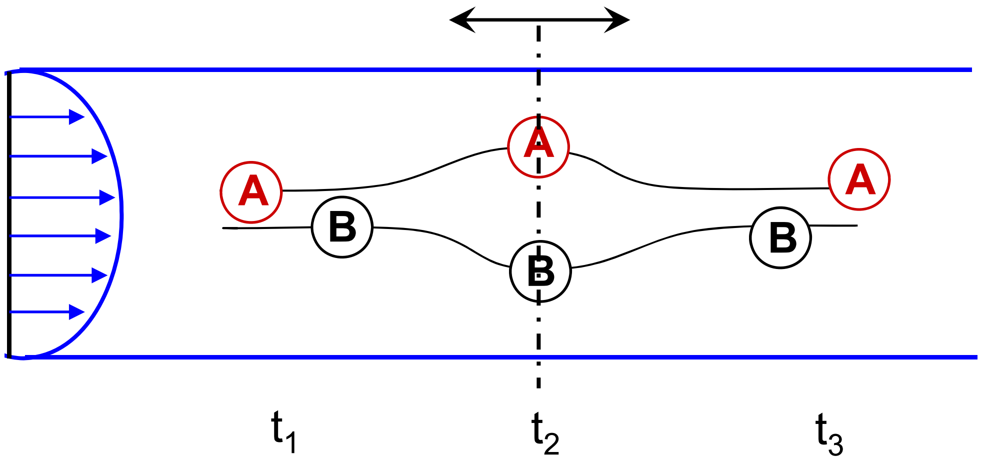


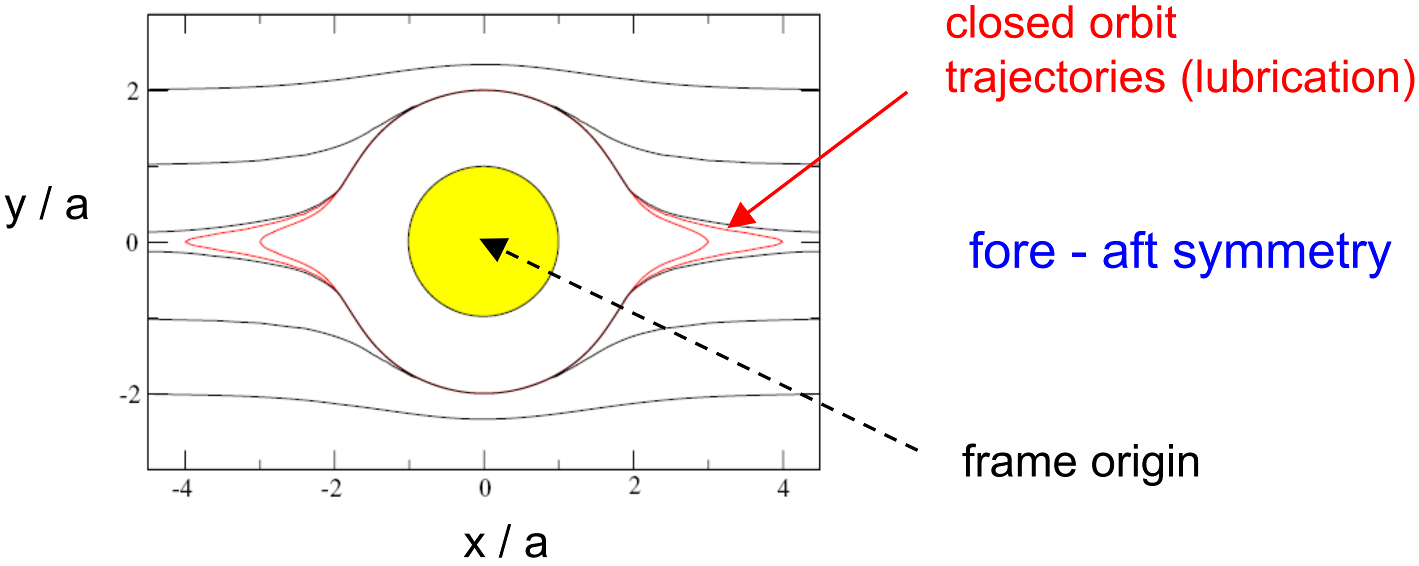
- Drag - along effect strongest for in - line sedimentation
- Lubrication plays no role for motions considered here (**Rotne – Prager o.k. for r > 5a**)



- Lubrication important for relative pair motion close to contact

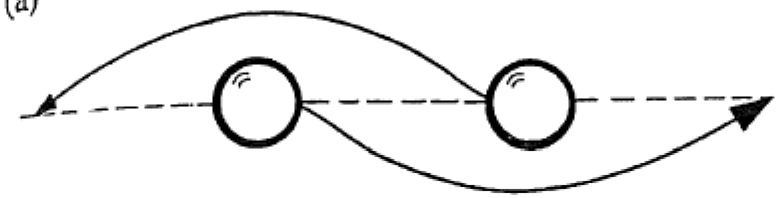
Two – sphere „collisions“





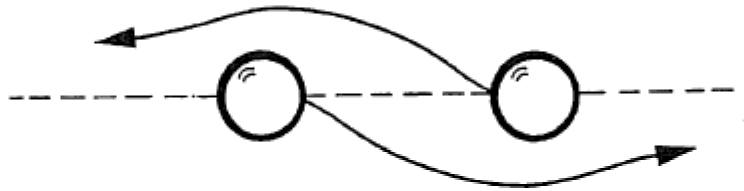
- Fore - aft symmetry can be broken, e.g., by hydrodynamic three – sphere collisions

(a)



Ideal spheres, HI only

(b)



spheres with surface roughness
(lateral displacement after „collision“)

6. Smoluchowski & Stokes-Liouville dynamics

- Many-particle diffusion equation
- Dynamic simulations

6.1 Many- particle 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 Smoluchowski equation

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

Brownian motion $\propto$ T

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

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

$$\langle\Delta\mathbf{R}_i(\tau)\rangle = \sum_{j=1}^{N}\left[\boldsymbol{\mu}_{ij}^{tt}(X_0)\cdot\mathbf{F}_j(X_0) + k_B T\nabla_j\cdot\boldsymbol{\mu}_{ij}^{tt}(X_0)\right]\tau + o(\tau)$$

$$\langle\Delta\mathbf{R}_i(\tau)\,\Delta\mathbf{R}_j(\tau)\rangle_0 = 2k_B T\boldsymbol{\mu}_{ij}^{tt}(X_0)\tau + o(\tau)$$

← HI - coupling of displacements of i & j

- Stokes – Liouville equation for non-Brownian driven spheres

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

$$P(X, t \to \infty) \to P_{stat}(X) \ \ \mathbf{?}$$

- Forward integration schemes based on:

$$\mathbf{R}_i(t_0+\tau) = \mathbf{R}_i(t_0) + \sum_{j=1}^{N} \left[\boldsymbol{\mu}_{ij}^{tt}(X_0) \cdot \left(\mathbf{F}_j^I(X_0) + \mathbf{F}_j^e(X_0) \right) \right] \tau + o(\tau)$$

- **Non-linear coupling: HI ↔ microstructure (PDF)**

How to calculate correlation functions

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

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

- Density fluctuations: $f(X) = g(X) = \int d^3r \exp\left(i\mathbf{q}\cdot\mathbf{r}\right) \sum_{l=1}^{N} \delta\left(\mathbf{r} - \mathbf{R}_l\right)$
- **Dynamic structure factor** measured in dynamic light scattering (→ Roberto Piazza)

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

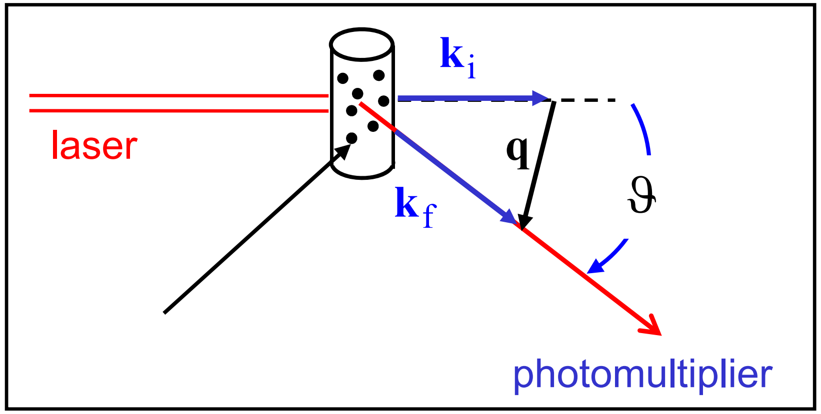
7. Collective diffusion & sedimentation

- Hydrodynamic function
- Sedimentation
- Intrinsic Convection

7.1 Hydrodynamic function

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

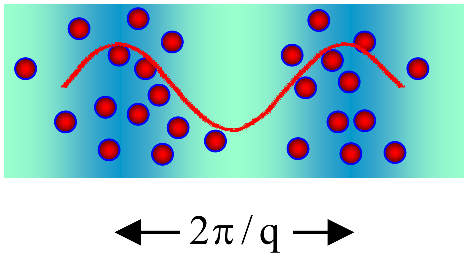
$$S(q, t \ll \tau_D) \approx S(q)\exp\left[-q^2 D(q) t\right]$$



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

short - time diffusion function

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



H(q) = 1 without HI

Physical meaning: generalized sedimentation coefficient

- Homogeneous system with spatially periodic force acting on each sphere:

$$\mathbf{F}_j = \hat{\mathbf{q}} F^e \exp\left[-i\,\mathbf{q}\cdot\mathbf{R}_j\right]$$

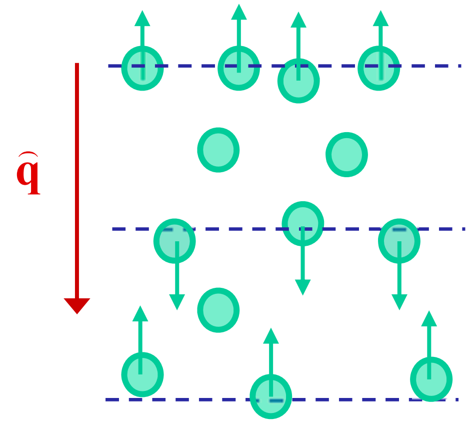
weak external force on sphere j

$$\langle V(q)\rangle = \left\langle \frac{1}{N}\sum_{j=1}^{N} \hat{\mathbf{q}}\cdot\mathbf{V}_j \exp\left[i\,\mathbf{q}\cdot\mathbf{R}_j\right]\right\rangle$$

mean (short - time) response

$$\langle V(q)\rangle = H(q)\,\mu_0\,F^e$$

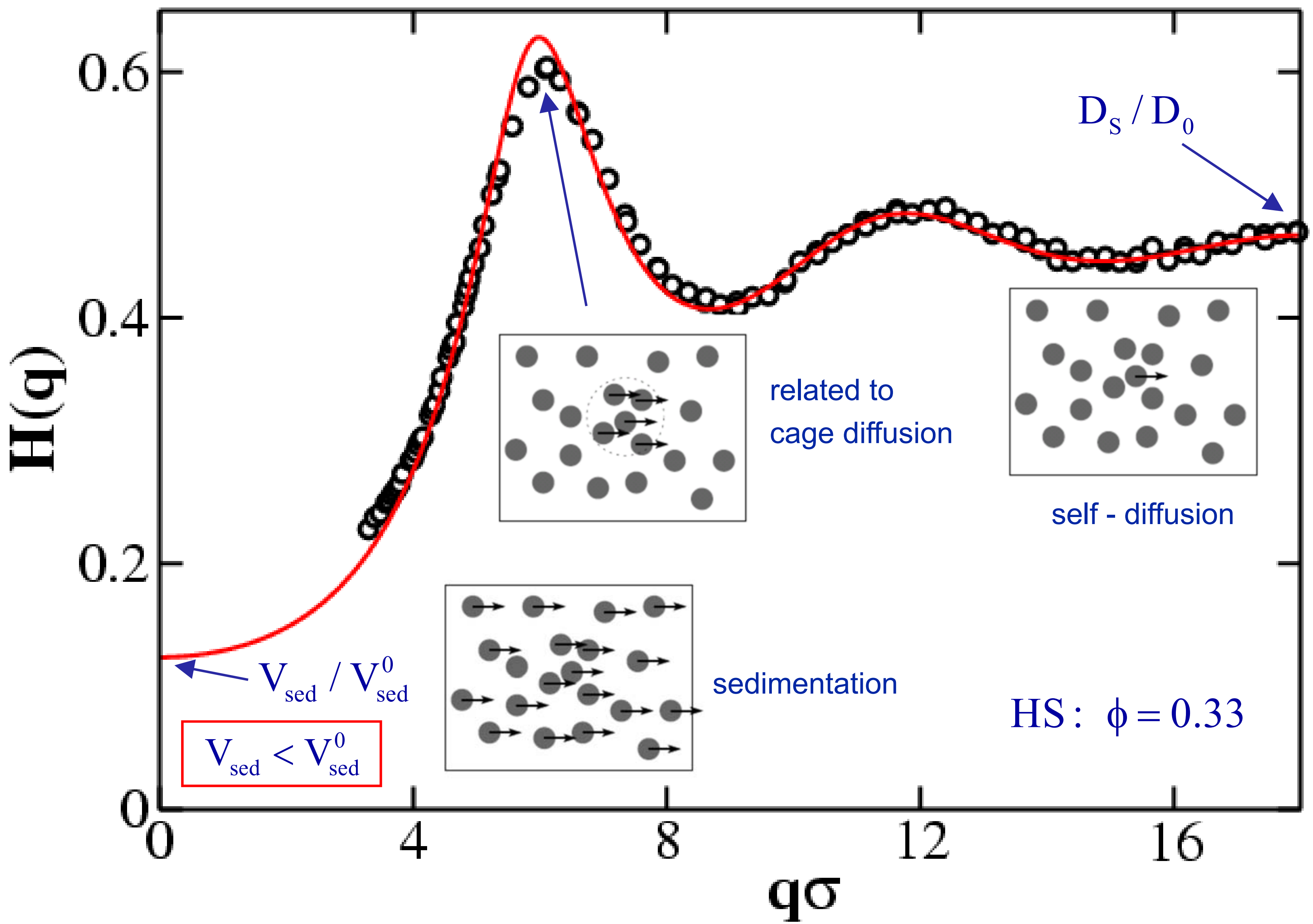
$$V_{sed}^{0} = \mu_0 F^e$$



$$\lim_{q\to 0}\langle V(q)\rangle = V_{sed} - \langle \mathbf{u}_{susp}(\mathbf{r};X)\rangle$$

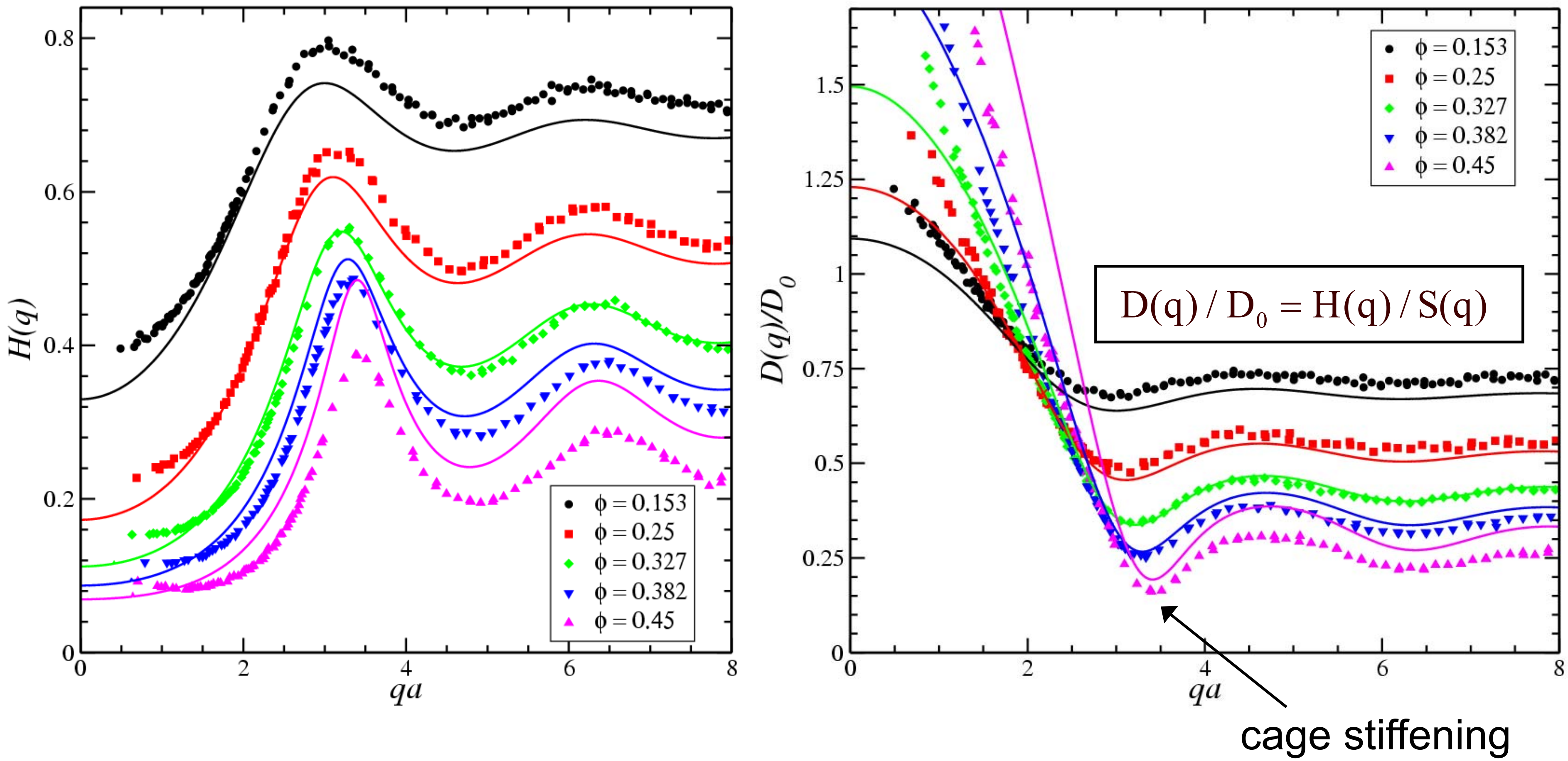
- **mean suspension velocity**

- **Lab frame** = zero volume flux frame
- Sedimentation velocity in
  zero - volume flux reference system



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

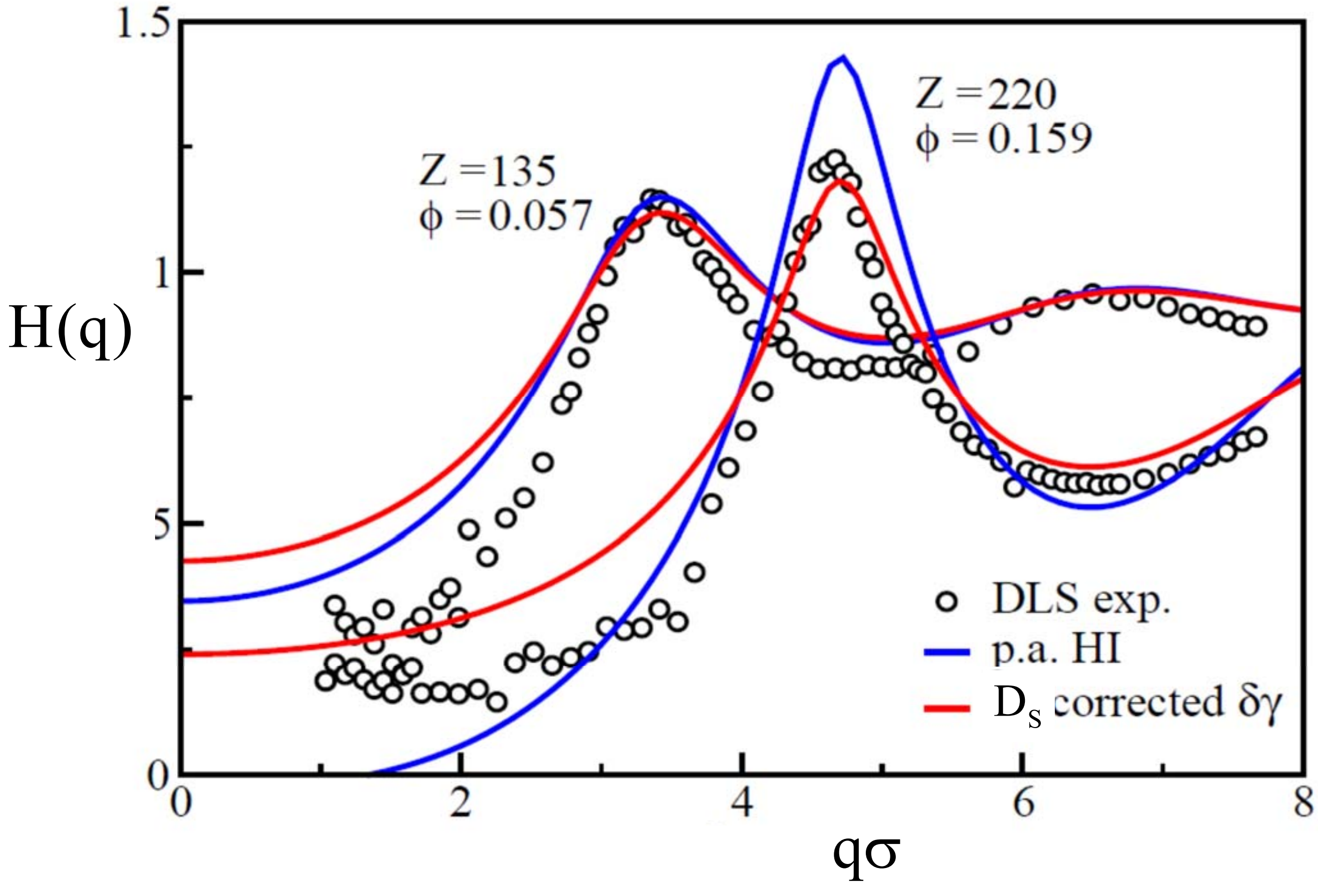
Hard spheres – hydrodynamic & diffusion function



- Symbols: accelerated Stokesian dynamics simultion method
- Lines: analytic theory (so-called uncorrected δγ – theory)

A.J. Banchio and G. Nägele, J. Chem. Phys. **128**, 2008

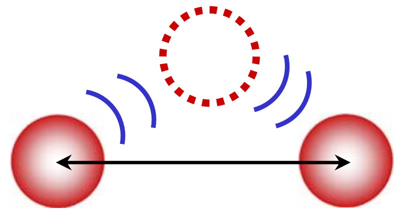
Charged colloidal spheres: Experiment and theory



HI shielding:

$$\mathbf{u(r)} \sim \frac{1}{\eta_{eff}(\phi)\, r}$$

Nägele et al.
PRL **96**, 108303 (2006)

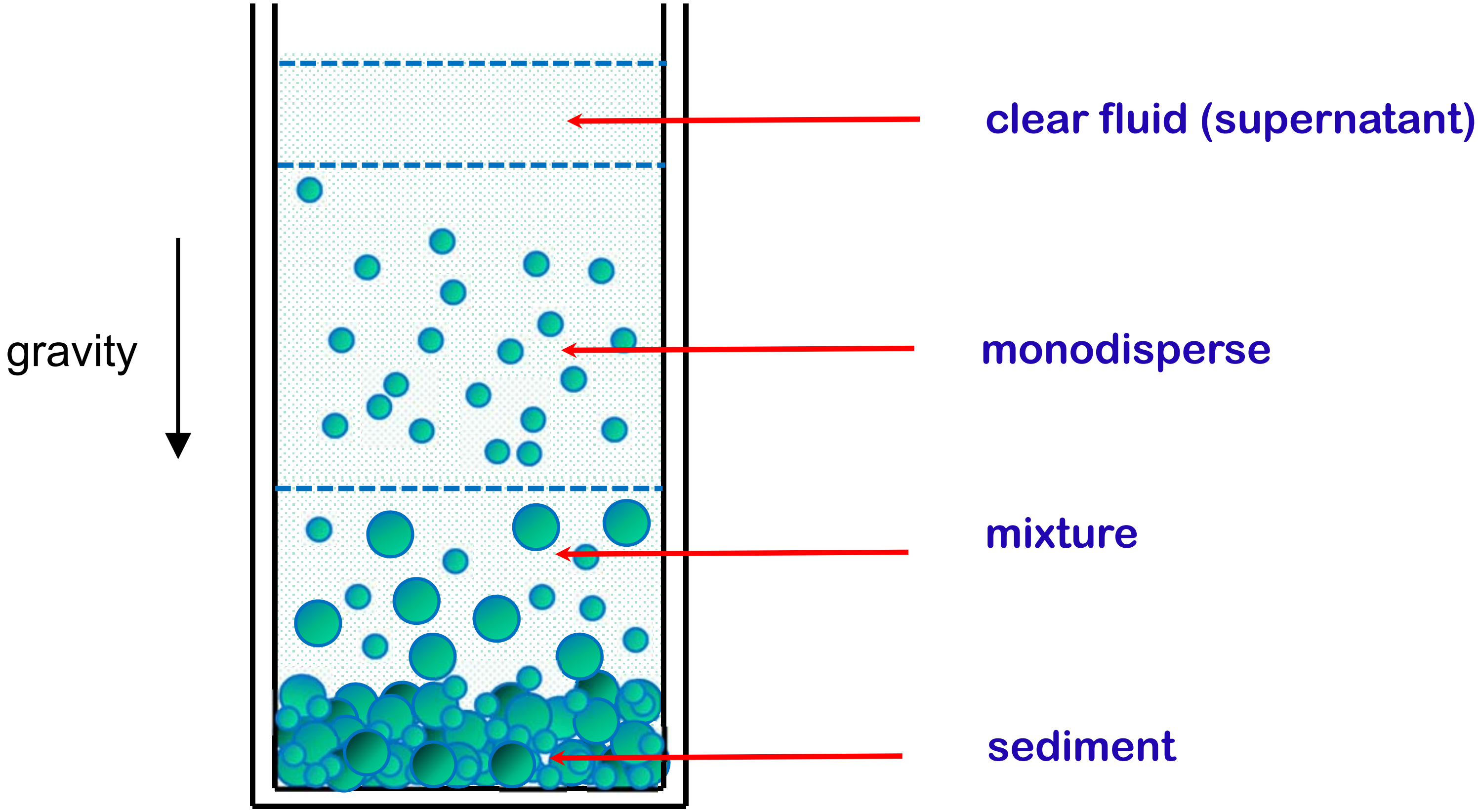


- Pairwise additive HI: good for low ϕ only, disregards HI shielding
- Corrected δγ - theory: close to exp. & simulation throughout liquid phase

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., in press (2012)

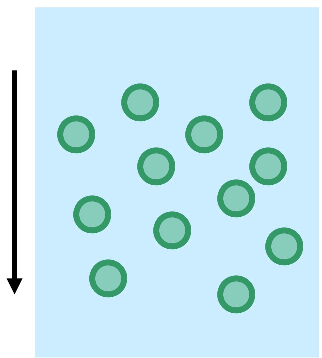
7.2 Sedimentation



Brownian sedimentation

- Slow settling of colloidal **Brownian spheres** starting from homogeneous state

$$\mathbf{F}^e = F^e\,\hat{\mathbf{q}}$$



$$V_{sed}^0 = \mu_0^t F^e$$

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

- Sedimenation Peclet – #::

$$\text{Pe} = \frac{\text{diffusion time}}{\text{sedimentation time}} = \frac{\tau_D = \sigma^2 / D_0}{\tau_{sed} = \sigma / V_{sed}^0} \ll 1$$

$$P_{in}(X, t=0) \underbrace{\rightarrow}_{t \gg \tau_D} \begin{cases} P_{st}(X) = P_{eq}(X) & \text{zero or pairwise-additive HI} \\ P_{st}(X) \neq P_{eq}(X) & \text{3 - and more-body HI} \end{cases}$$

equil. distribution for zero gravity force

- Find stationary & homog. pdf solution of GSE under constant external force **F**

$$\frac{\partial}{\partial t} P_{st}(X) = \hat{O}_{sm}(X) P_{st}(X) = 0$$

$$\mathbf{V}_{sed} = \left\langle \frac{1}{N} \sum_{i=1}^{N} \mathbf{v}_i(X,t) \right\rangle_{st} = \left\langle \frac{1}{N} \sum_{i,l=1}^{N} \boldsymbol{\mu}_{il}^{tt} \cdot \left[\underbrace{\mathbf{F}_l^I - k_B T \nabla_l \ln P_{st}(X)} + \mathbf{F}^e \right] \right\rangle_{st}$$

long-time (memory) part of V_{sed}
vanishes for PA - HI where $P_{st} = P_{eq}$

- Linear response stationary solution:

$$P_{st}(X) = P_{eq}(X) \left[1 - \beta \mathbf{F}^e \cdot \int_0^\infty du\, e^{\hat{O}_B^0 u} \sum_{j=1}^{N} \hat{O}_B^0 \mathbf{R}_j \right] + O((\mathbf{F}^e)^2)$$

$$\hat{O}_B^0 = \hat{O}_B(\mathbf{F}^e = 0)$$

$$\mathbf{V}_i^I = \hat{O}_B^0 \mathbf{R}_i$$

adjoint Smoluchowski operator without external force

- Mean sedimentation velocity at small Peclet numbers:

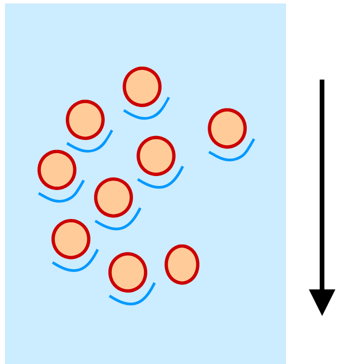
$$\frac{V_{sed}}{V_{sed}^{0}} = \left\langle \frac{1}{\mu_0^t} \sum_{i,l=1}^{N} \hat{\mathbf{q}} \cdot \boldsymbol{\mu}_{il}^{tt} \cdot \hat{\mathbf{q}} \right\rangle_{eq} - \text{memory part}$$

$H(q=0)$: short-time part

zero for PA-HI or small
Reason: mean motion in same direction

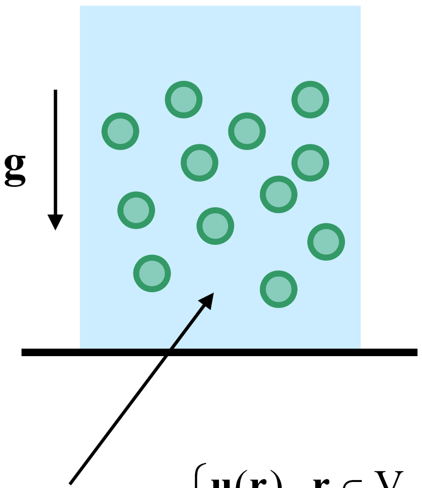
- Smoluchowski's paradoxon :

$$H(q=0) = 1 + \underbrace{n \int d\mathbf{r}\, g(r)\, \hat{\mathbf{q}} \cdot \omega_{12}^{RP}(\mathbf{r}) \cdot \hat{\mathbf{q}}}_{\to \infty} + \text{regular part}$$



?

Resolution: macroscopic solvent backflow due to container bottom



$$\mathbf{u}_{susp}(\mathbf{r};X) = \begin{cases} \mathbf{u}(\mathbf{r}), & \mathbf{r} \in V_{fluid} \\ \mathbf{V}_i, & \mathbf{r} \in V_{particle} \end{cases}$$

- consider container bottom explicitly (Mazur & van Saarlos, ´78)
- locallity of transport coefficients (Felderhof, Cichocki, ´80)
- use zero volume flux condition for planes ⊥ to $\mathbf{F}^e$ (Batchelor, ´72)

$$\int dS_{\perp} \langle \mathbf{u}(\mathbf{r};X) \rangle_{st} = 0$$ rest frame of container

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

- use that : $V_{sed} - \langle \mathbf{u}_{susp}(\mathbf{r};X) \rangle = V_{sed}^0 \lim_{q\to 0} H(q) \neq V_{sed}^0\, H(q=0)$

relative to ensemble averaged volume flow velocity, then

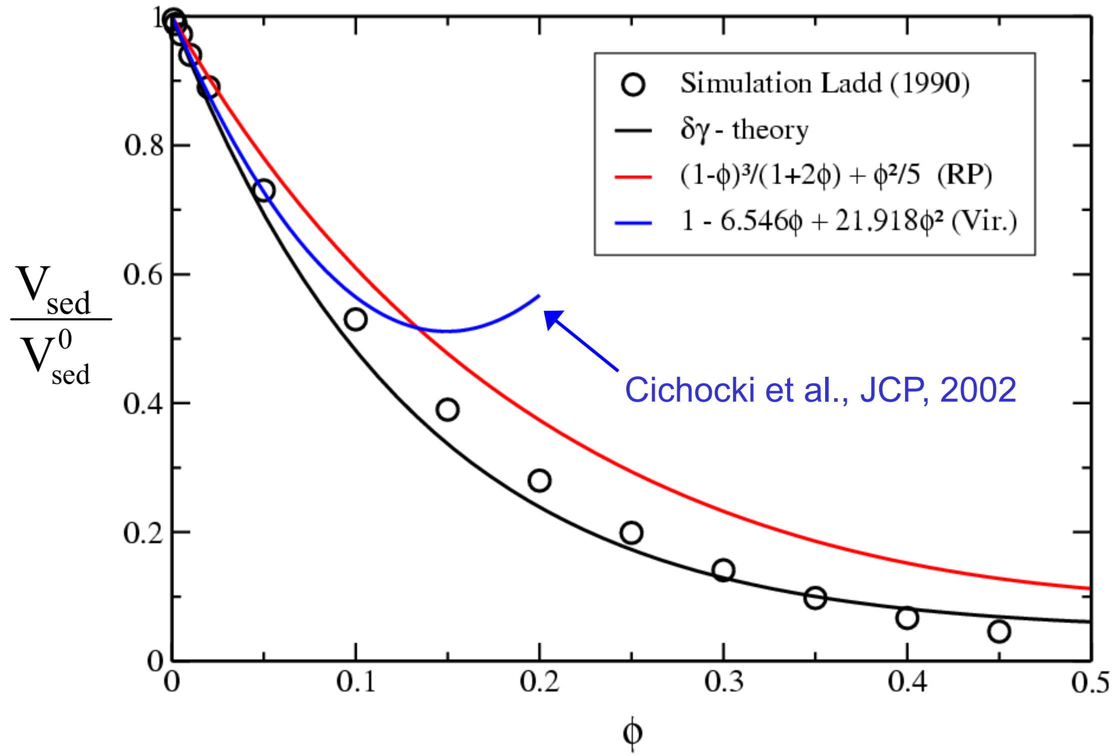
container-shape & position independent (c.f. intrinsic convection)

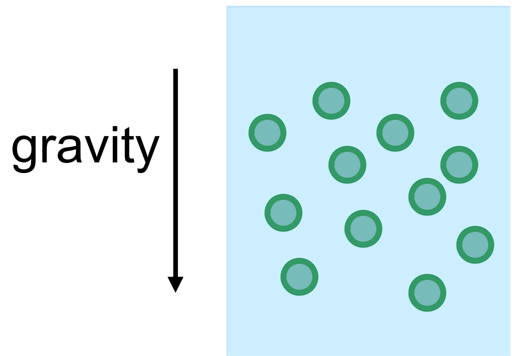
- (Short-time) sedimentation on Rotne - Prager level (zero volume velocity frame)

$$\frac{V_{sed}^{short}}{V_{sed}^{0}} = 1 - \phi \left[5 + \underbrace{12 \int_1^\infty dx\, x\, (1 - g(x;\phi))}_{\text{known analytically for hard spheres in PY}} + \frac{15}{8} \int_1^\infty dx\, \frac{g(x;\phi)}{x^2} \right] \qquad x = r/2a$$

$$\left(\frac{V_{sed}^{short}}{V_{sed}^{0}} \right)_{HS} = \begin{cases} (1 - \phi)^3 / (1 + 2\phi) + \frac{1}{5}\phi^2 \approx 1 - 5\phi + \frac{66}{5}\phi^2 & \text{in RP-PY} \\ 1 - 6.546\,\phi + 21.918\,\phi^2 + ? & \text{exact (Cichocki et al., '02)} \end{cases}$$

Sedimentation of Brownian hard spheres





Banchio & Nägele, JCP **127**, 2008

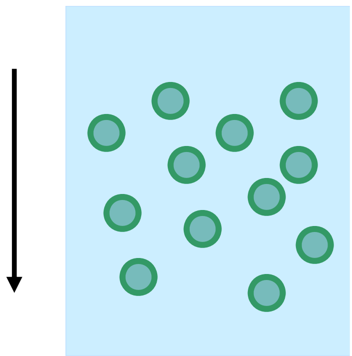
$$V_{sed}^{short} / V_{sed}^{0} = 1 - 6.546\,\phi + 21.918\,\phi^2 + \ldots$$

$$V_{sed}^{RP} / V_{sed}^{0} = \frac{(1-\phi)^3}{1+2\,\phi} + \frac{\phi^2}{5}$$

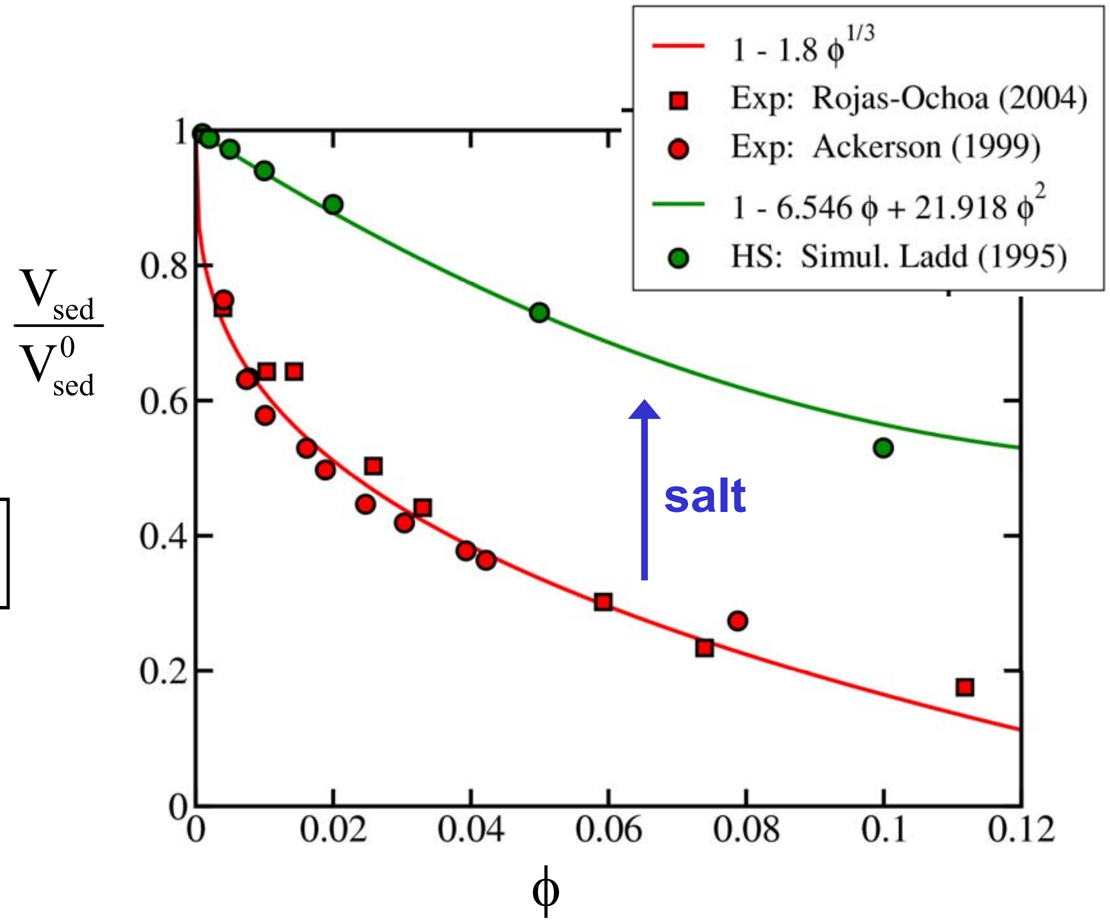
- RP far - field HI
- PY - g(r)

Sedimentation only weakly affected by near-field HI

Sedimentation of Brownian charged particles

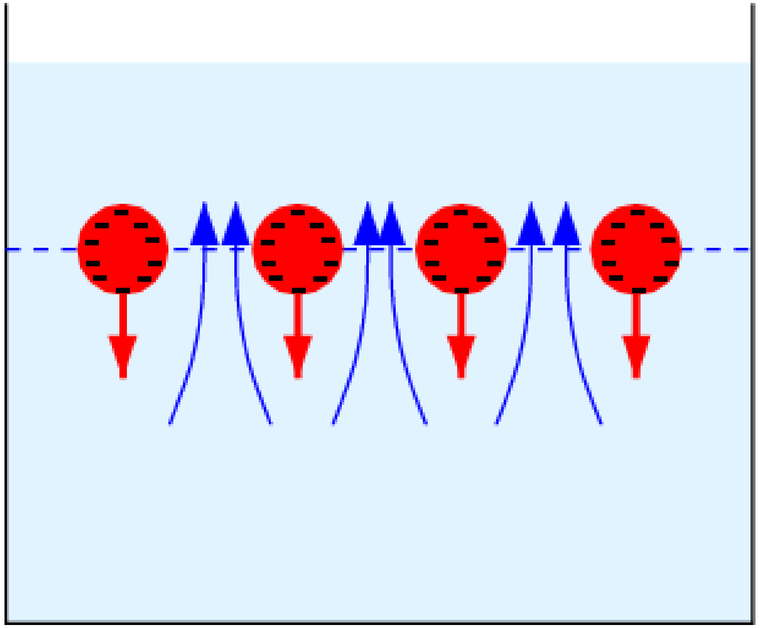


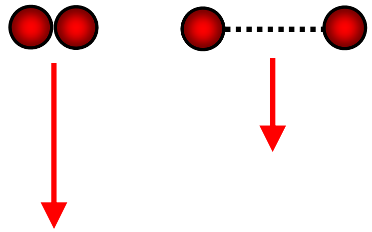
$$V_{sed} / V_{sed}^0 \approx 1 - 1.8\phi^{1/3}$$



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

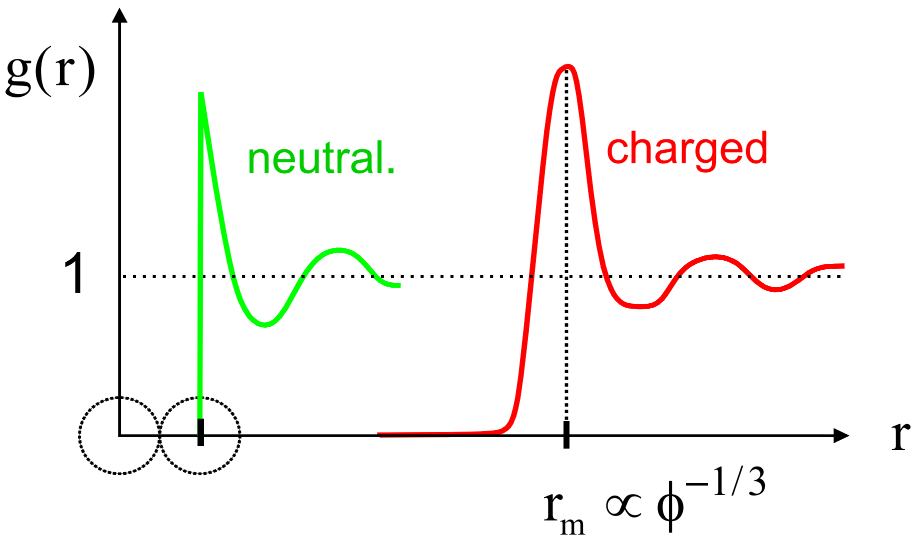
Watzlawek & Nägele; JCIS **214** (1997)





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

Pressure gradient drives homogeneous mean fluid backflow



- Increased friction with backflowing fluid

7.3 Intrinsic convection

$$\bar{V}_{sed} = V_{sed}(x) - \langle u \rangle_{st}(x) = V_{sed}^{0}\left(1 - 6.55\phi + O(\phi)^2\right)$$

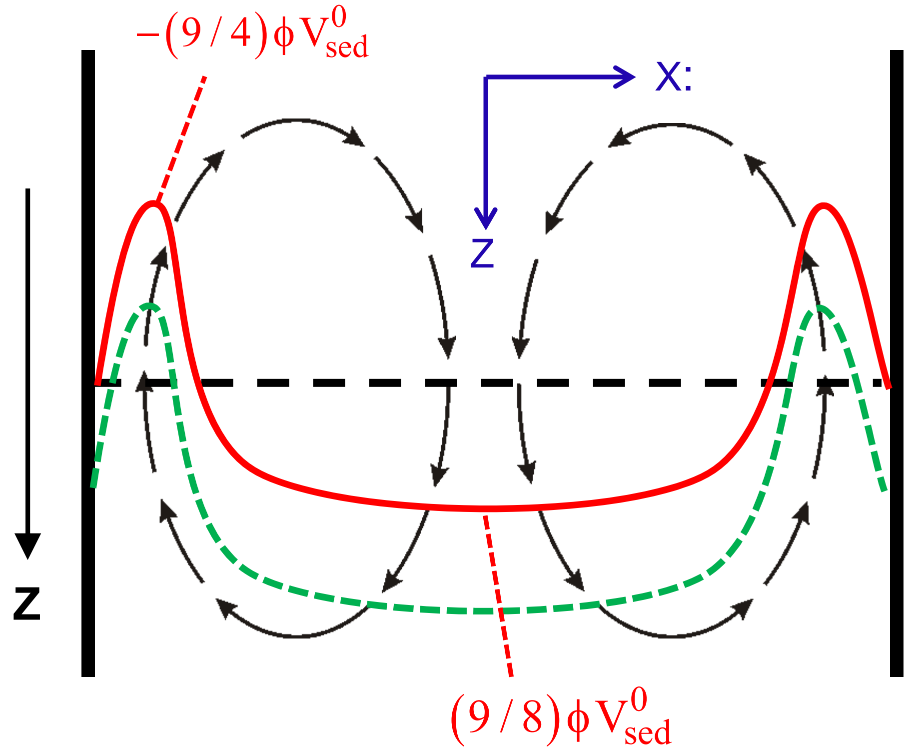
$$-\nabla \langle p \rangle_{st}(x) + \Delta \langle \mathbf{u} \rangle_{st}(x) + \langle \rho \rangle_{st}(x)\mathbf{g} = \mathbf{0}$$

$$\langle \rho \rangle_{st}(x) = \begin{cases} \rho_f & \text{near wall } \sim a \\ \phi\rho_p + (1-\phi)\rho_f & \text{in bulk} \end{cases}$$

$$\langle u \rangle_{st}(x) = \phi V_{sed}(x) + (1-\phi) u_B(x)$$

$\langle u \rangle_{st}(x = \pm L/2) = 0$ wall rest frame

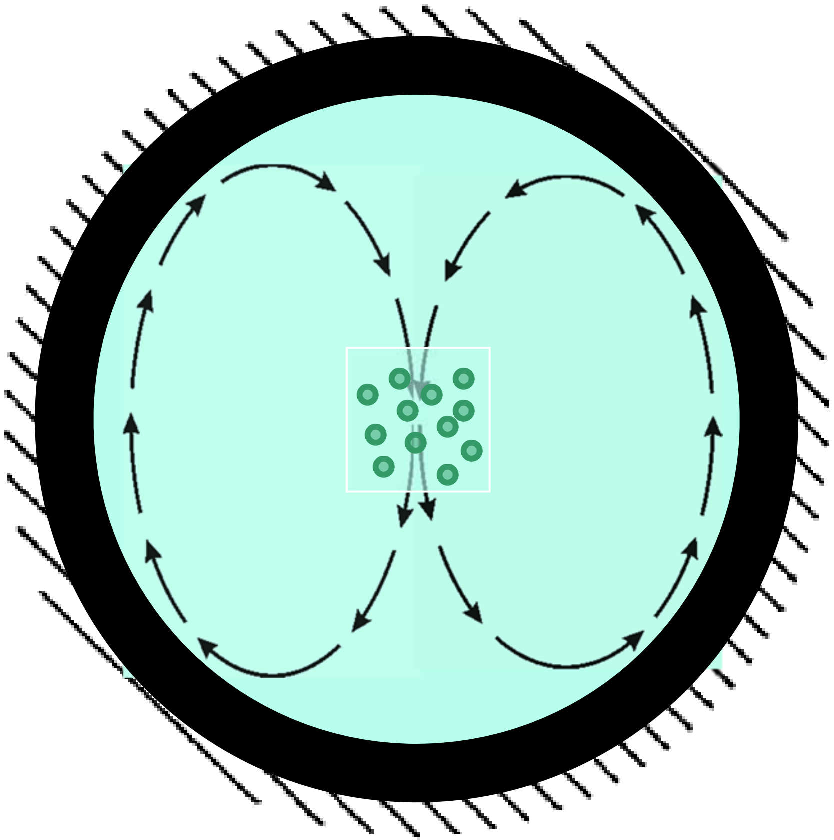
$$\frac{1}{L}\int_{-L/2}^{L/2} \langle u \rangle_{st}(x)\, dx = 0$$



- Particle - depleted buoyant layer near walls drives upward suspension flow
- Lateral average of $V_{sed}(x)$ gives the true (relative) sedimentation velocity

D Bruneau, Phys. Fluids **8** (1995), and section 7.3 in book by Jan Dhont

Rest frame of spherical rigid container with radius R → ∞



C.W.J. Beenakker & P. Mazur, Phys. Fluids **28** (1985)

$$V_{sed}(\mathbf{o}) = V_{sed}^0\left(1 - 3.55\phi + O\left(\phi^2\right)\right)$$

$$\langle u\rangle_{st}(\mathbf{o}) = 3\phi V_{sed}^0 + O\left(\phi^2\right)$$

$$u_B(\mathbf{o}) = -\frac{\phi}{1-\phi} V_{sed}^0$$

$$\frac{1}{V_{vess}} \int_{V_{vess}} d^3r\, \mathbf{u}_{susp}(\mathbf{r}, X) = 0$$

In rest frame of vessel
for incompresible fluid & particles:

- Weak intrinsic convection disappears at higher concentrations

Y. Peysson & E. Guazzelli, Phys. Fluids **10** (1998)

7.4 Sedimentation of large non-Brownian particles

- Stokes – Liouville equation for **driven system** of non - Brownian particles (T - indep.):

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

$$P(X, t \to \infty) \to P_{stat}(X) \ \ \mathbf{?}$$

- **T - limit existent ?**

- Intricate non-linear coupling of microstructure (pdf) and HI, both dependent on X.
- Instabilities at higher concentrations and strong driving (chaotic trajectories).
- Simulations with large particle numbers are needed.

- Locallity of V_{sed} presupposed: $V_{sed} - \langle u \rangle_{st} = \left(1 - 3.87\,\phi + O(\phi)^2\right)$

$g_{st}^{HS}(r) \neq \Theta(r - 2a)$ transient closed pairs formed (cf. infinite-Peclet viscosity)

$n \int dV \left[g_{st}^{HS}(r) - 1 \right] = -1$ B. Cichocki & K. Sadlej, Europhys. Lett. **72** (2008)

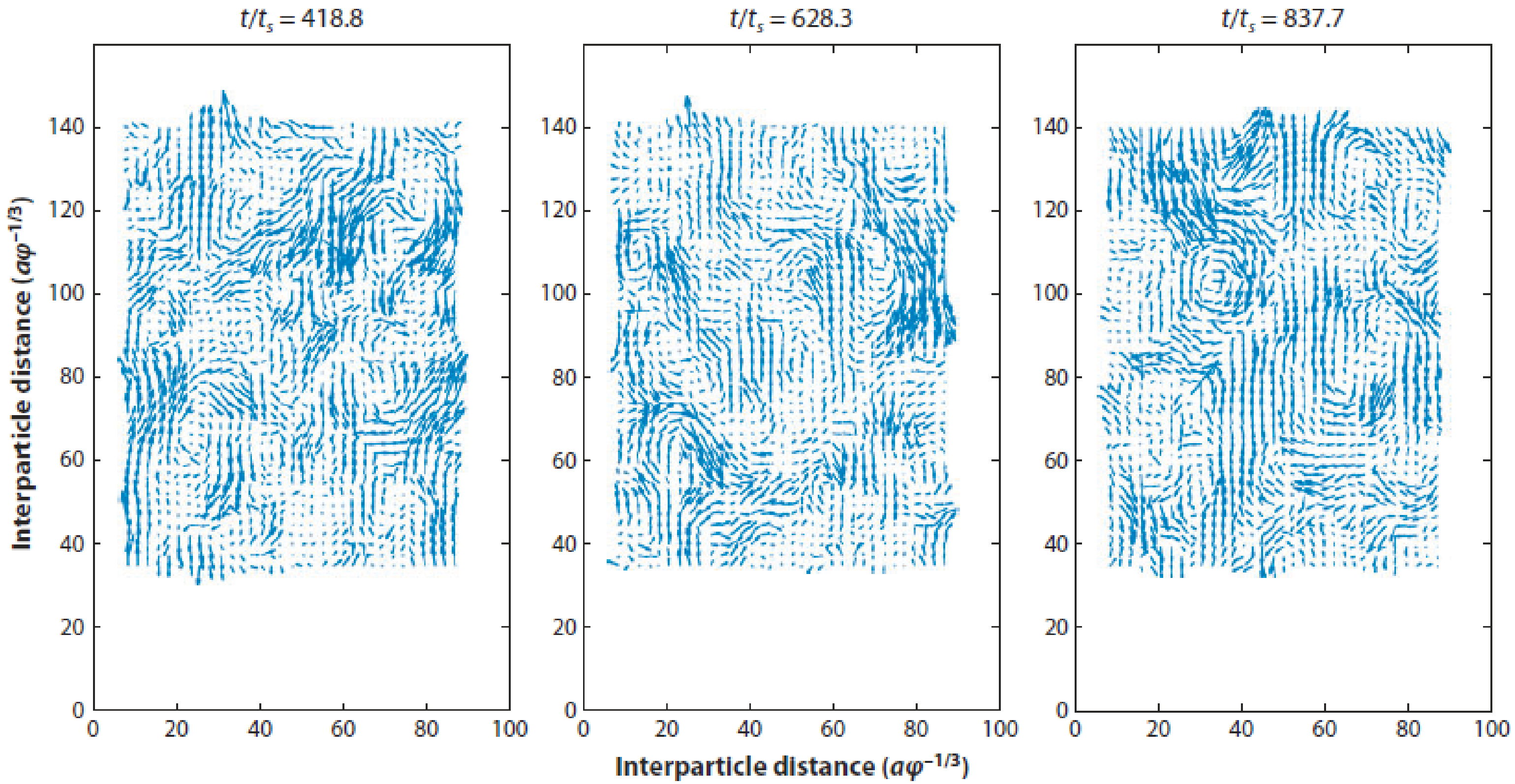


Figure 3

Dominance of the remaining smaller-scale fluctuations until the arrival of the upper sedimentation front. The velocity field is from particle image velocimetry sampling the entire cell cross section for a window covering the lower one-fourth of the cell height (Bergougnoux et al. 2003, Chehata Gómez et al. 2009). The timescale is the Stokes time $t_S = a/V_S$.

- Large - scale velocity fluctuations only transient
- Quasi - steady state of smaller-scale fluctuations of about 20 mean-particle distances
- Still open questions (stratification, side wall effects, locallity …)

taken from: E. Guazzelii and J. Hinch, Annu. Rev. Fluid Mech. **43**, 97 (2011)

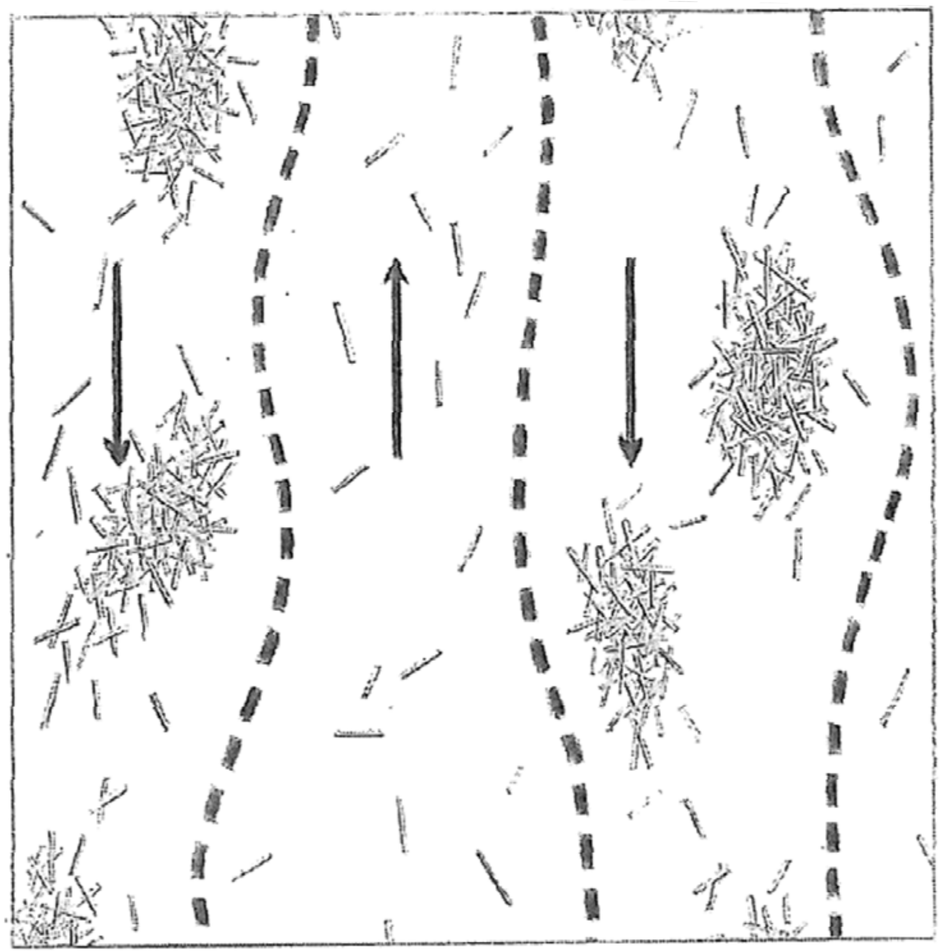


Figure 6.15 Sketch of the structural instability of a sedimenting suspension of fibers.

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

7.5 Gradient diffusion

- Gradient diffusion (Brownian particles):
  Condition: $q << q_m$

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

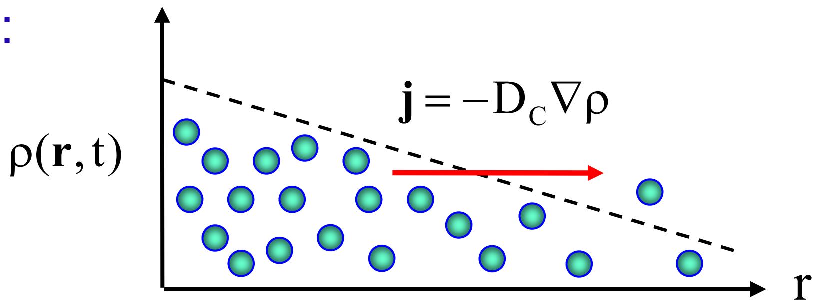
$$\frac{D_C}{D_0} = \lim_{q\to 0}\frac{H(q)}{S(q)} = \frac{V_{sed}/V_{sed}^0}{k_B T\left(\partial\overline{\rho}/\partial p_{osm}\right)_{T,\mu_s}}$$

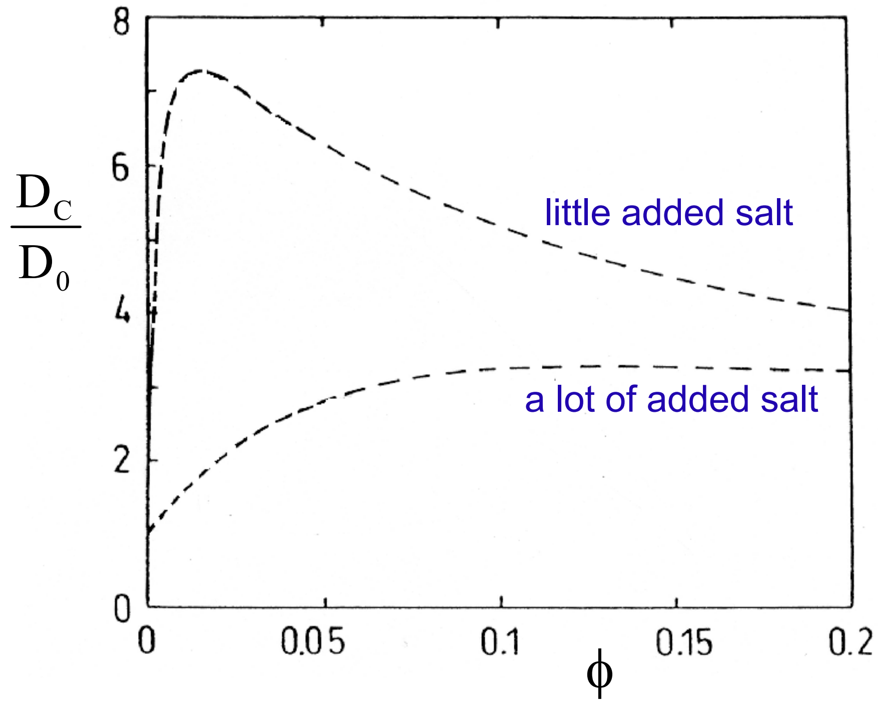
osmotic pressure

Hydrodynamic interaction : V_{sed}/V_{sed}^0

↕

Osmotic compressibility



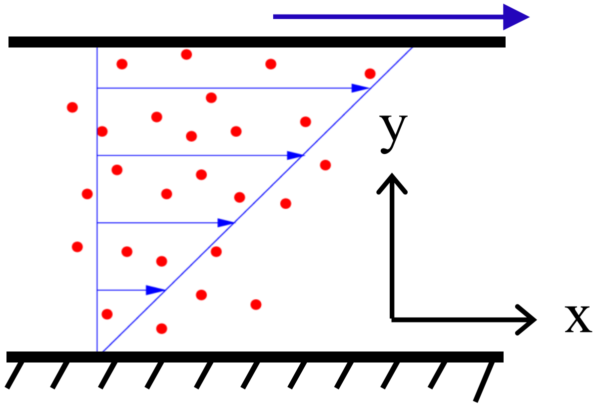


(G.Nägele, Phys. Reports 1995)

8. Suspension viscosity

- General properties
- Examples
- Shear thinning and thickening

8.1 General properties



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

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

- 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

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

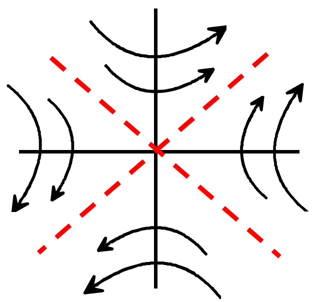
shear relaxation contribution (Δη) DI (Σ^I_{xy}) Brownian forces ∝ T (Σ^B_{xy})

- High - frequency viscosity part (HI only):

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

symmetric force dipole (stresslet)

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



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

- Shear – relaxation viscosity part:

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

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

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

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)

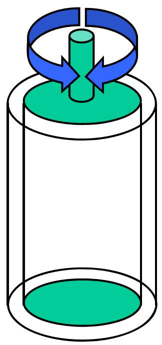
W.B. Russel, J. Chem. Soc. Faraday Trans. **2**, 80 (1984)

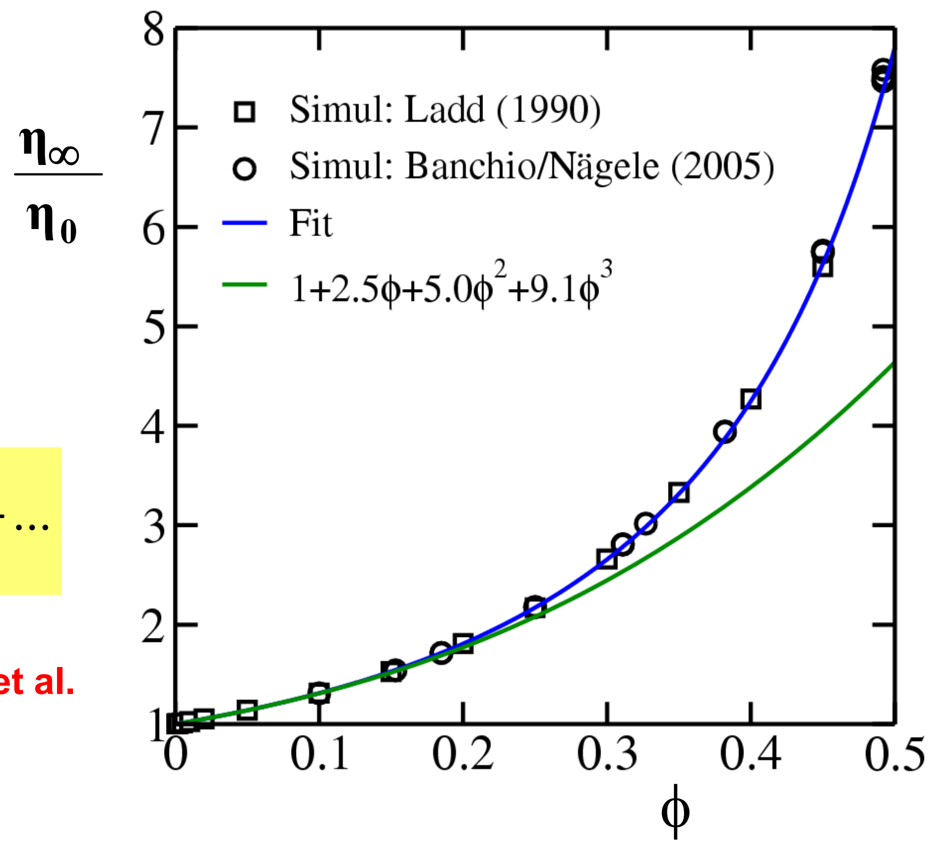
G. Nägele and J. Bergenholtz, J. Chem. Phys. **108** (1998)

8.2. Examples

- High-frequency viscosity of no - slip Brownian hard spheres

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





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

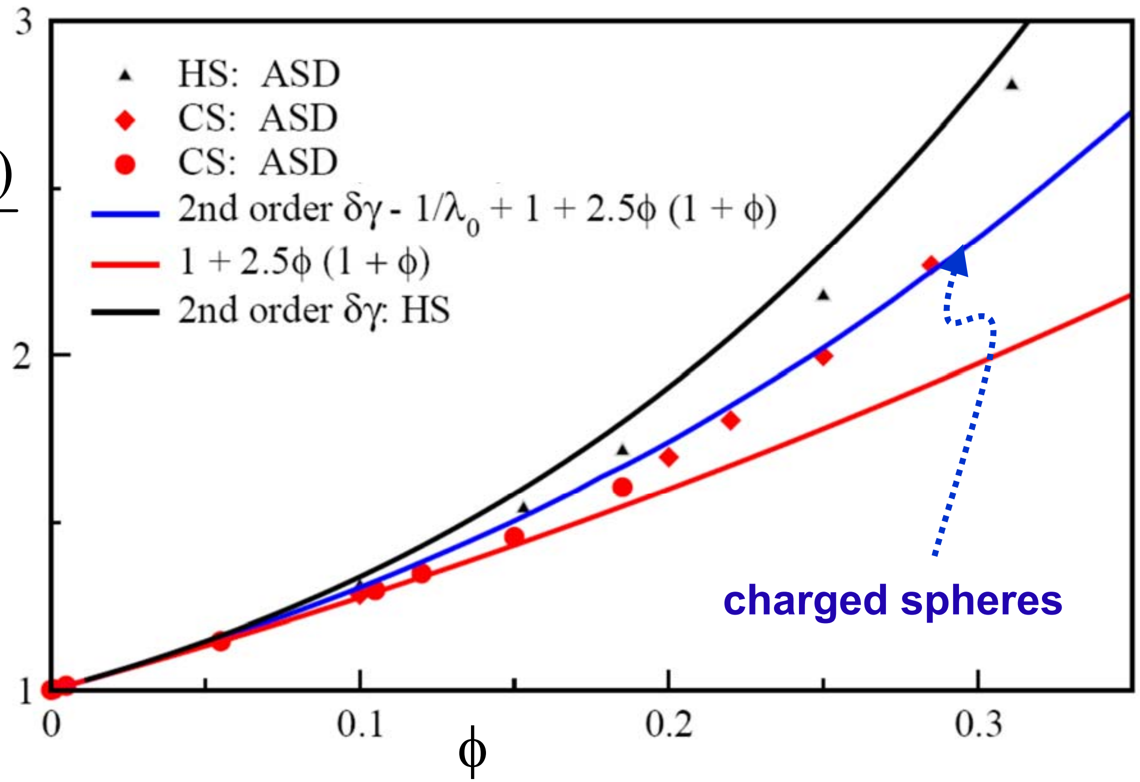
Einstein
1905: 1.0
1911: 2.5 (Hopf)

Batchelor & Green
(1972)

Cichocki et al.
(2003)

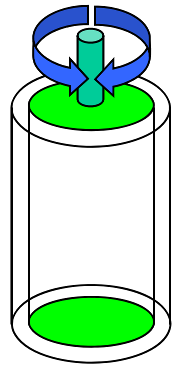
- Virial expansion in volume fraction applicable to lower concentrations only
- High frequency viscosity diverges at random closed packing: $\phi_{rcp} \approx 0.64$

High - frequency viscosity of charged Brownian spheres



$$\frac{\eta_\infty(\dot{\gamma}=0)}{\eta_0}$$

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

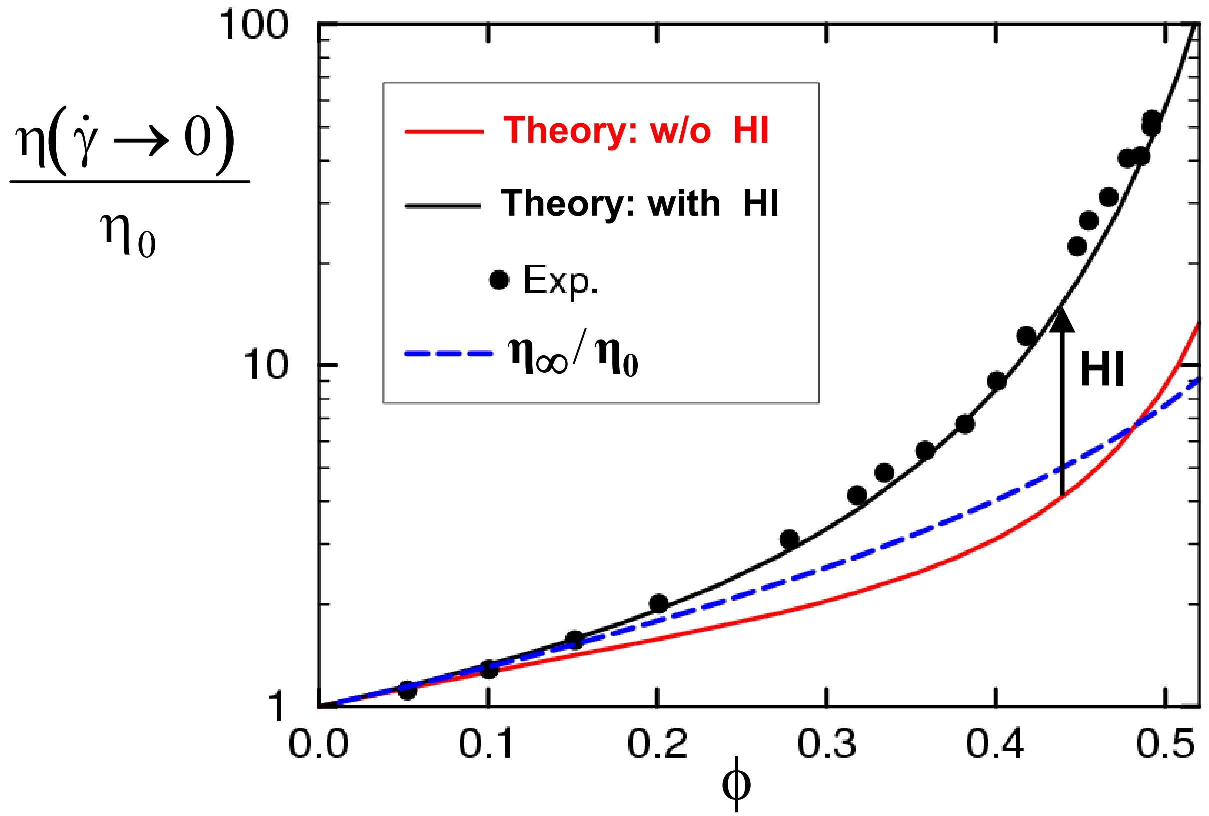


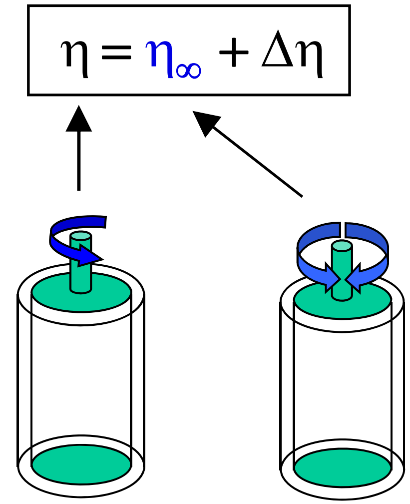
$$\eta = \eta_\infty + \Delta\eta$$

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

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

Steady-state versus high-frequency viscosity of hard spheres





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

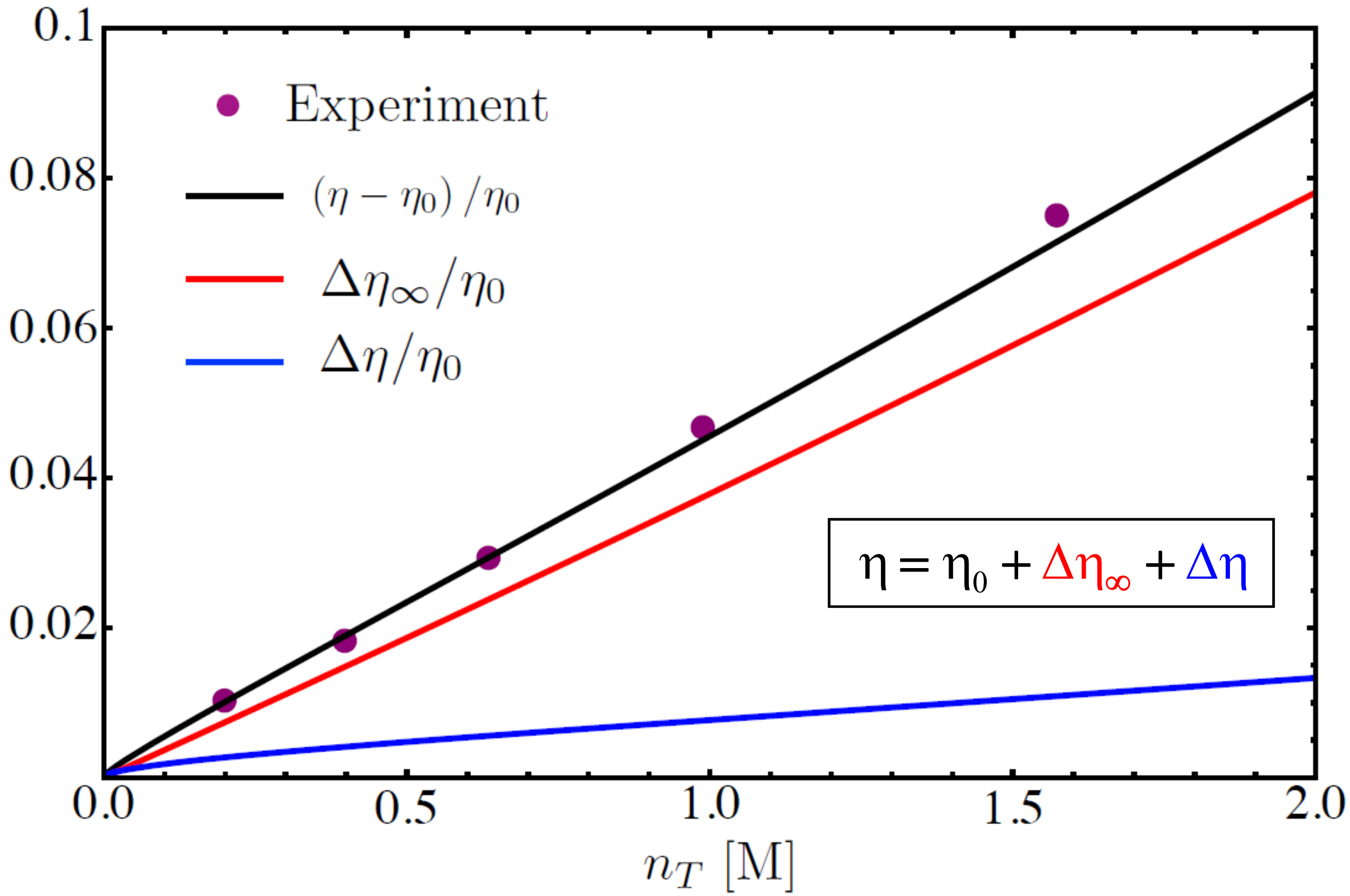
0.9 from Σ^B_{xy} $\left(\Sigma^I_{xy} = 0 \text{ for HS}\right)$

Batchelor (1972)

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

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

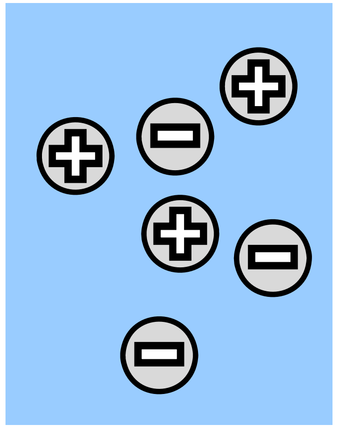
Viscosity of a 1 -1 electrolyte



NaCl in water

T = 25°C

$\bar{\sigma} = 3.6$ A

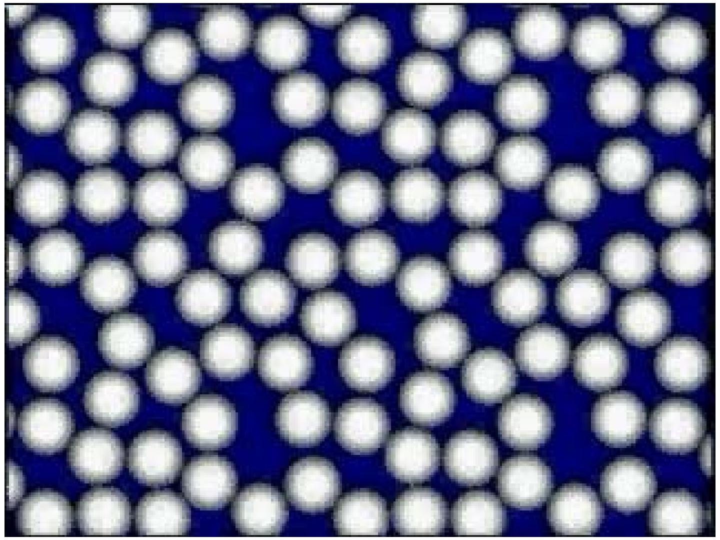


Mode - Coupling theory with HI: C. Contreras-Aburto and G. Nägele, J. Phys.: Condensed Matter, to appear (2012)

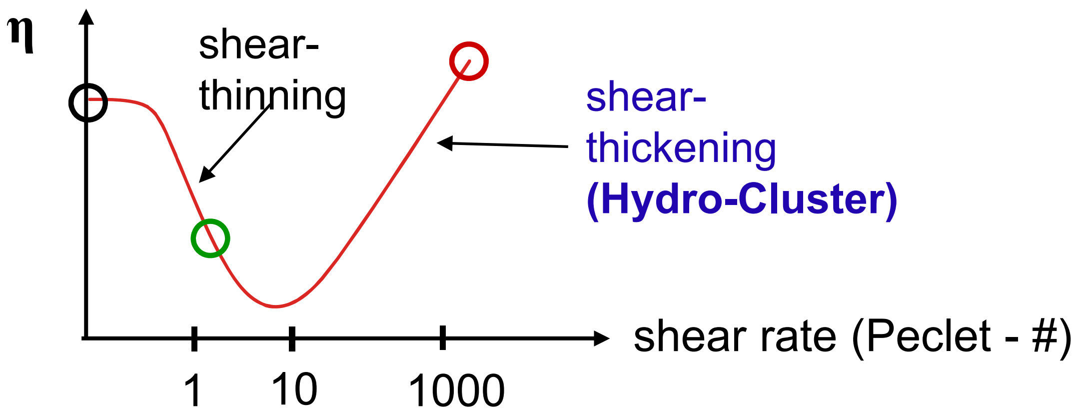
8.3 Shear-thickening and thinning

2D – Simulation: relative shear rate = 0.1, 10, 1000 (Peclet-number)

Without HI



With HI



$$\phi_A = 0.67$$

$$\phi_A^{rcp} = 0.82$$

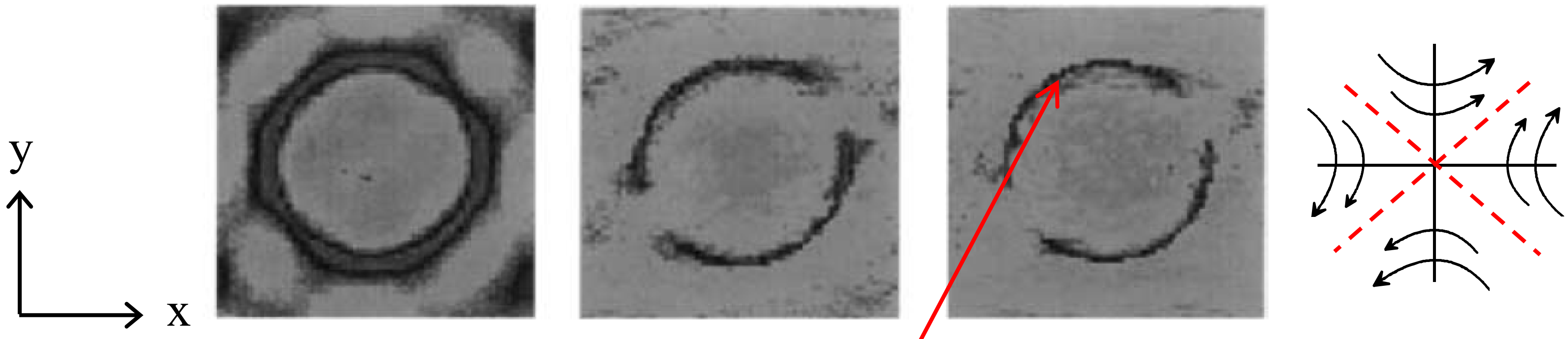
$$\phi_A^{crys} = 0.907$$

Foss und Brady

J. Fluid Mech **407** (2000)

Steady-state pair distribution function g(x,y): Brownian hard spheres

Taken from: J. Brady, Chem. Engineering Science **56**, 2921 (2001)



Pe = 0.1 10 1000

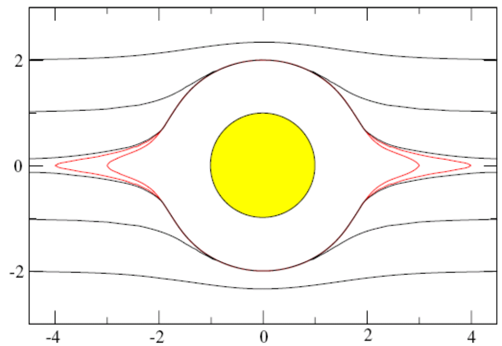
$g_{cont} = O(Pe)$

- Tight boundary layer (BD – convection) around compression axis
- Shear-thinning & thickening even to $O(\Phi^2)$

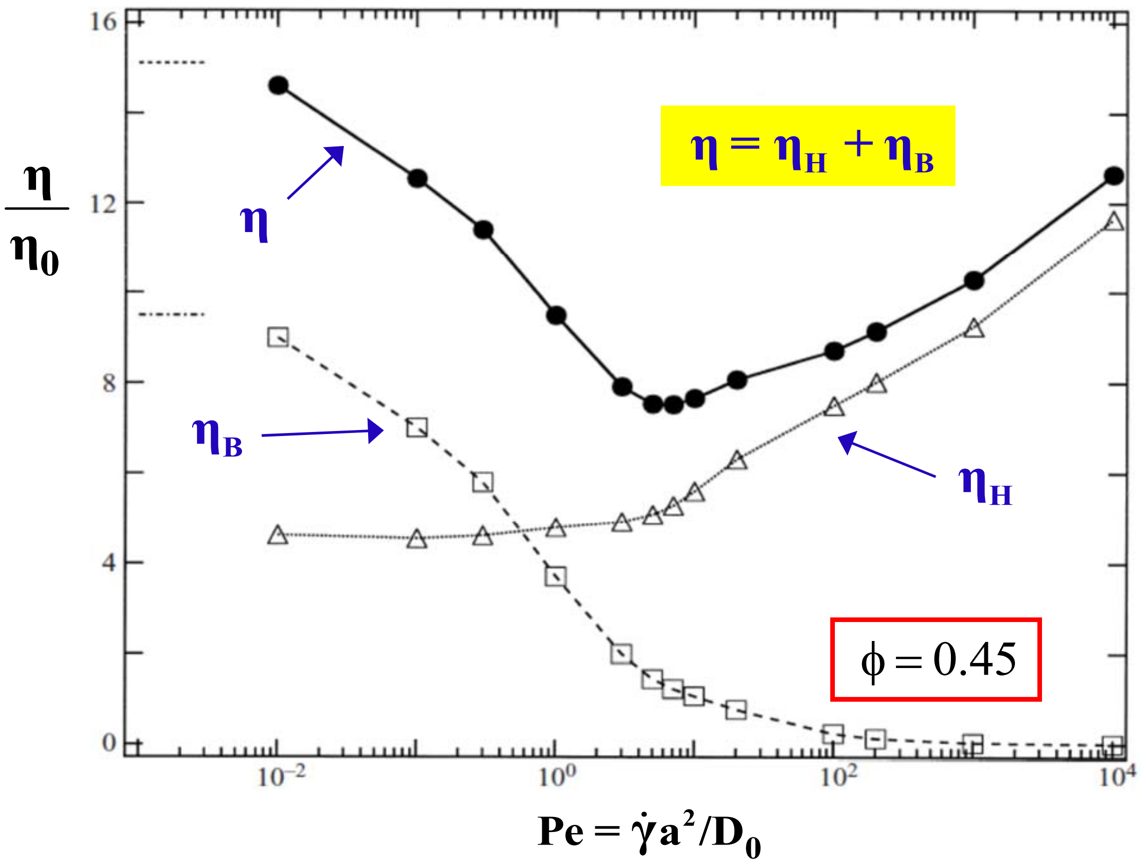
$$\eta(\dot{\gamma} \to \infty)/\eta_0 = 1 + 2.5\phi + 6.0\,\phi^2 + \ldots$$

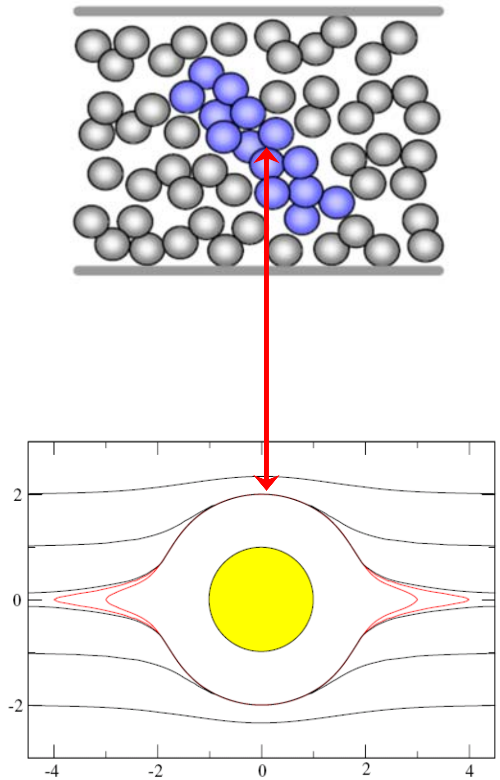
$$\eta(\dot{\gamma} = \infty)/\eta_0 = 1 + 2.5\phi + 6.95\phi^2 + \ldots(\text{pure strain})$$

Batchelor (1972)



Brownian hard spheres: simulation results



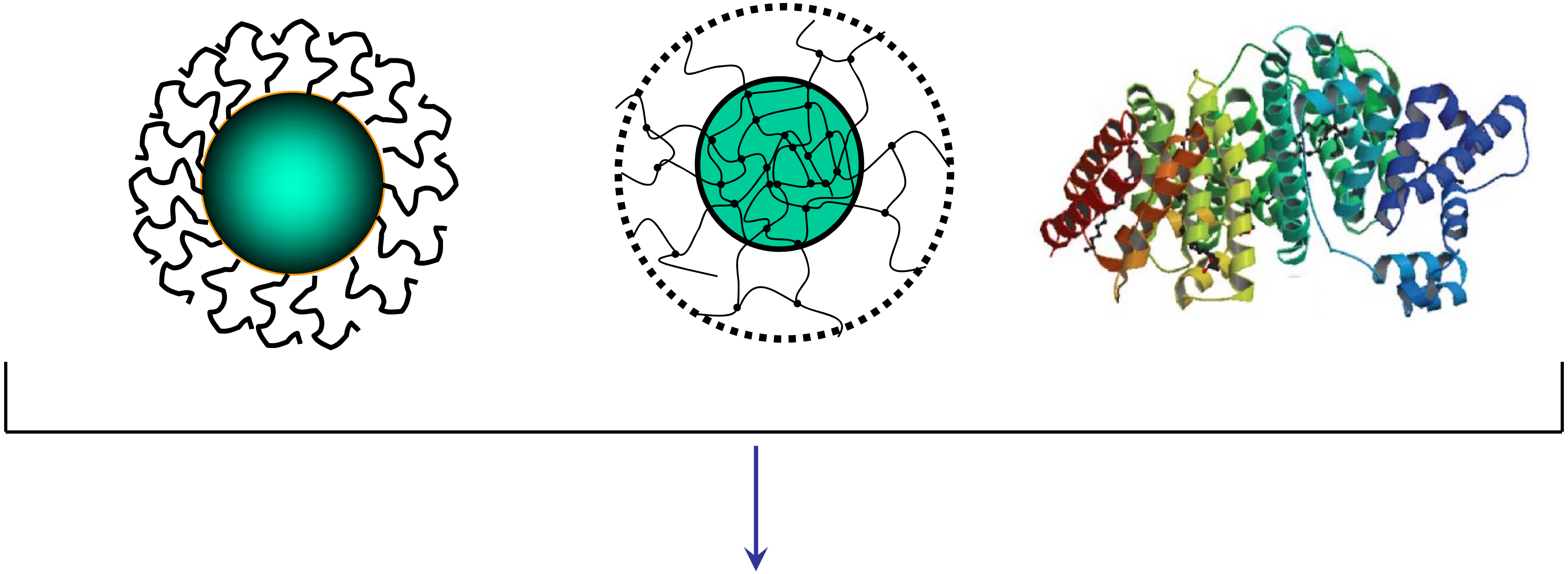


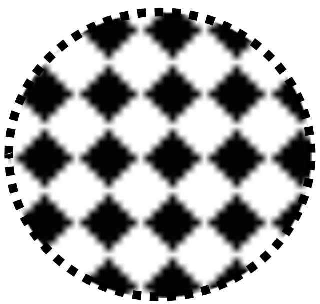
- Shear – thickening explained here by transient hydrocluster formation (lubrication)
- Brownian stress contribution ceases with increasing shear rate

taken from: Foss und Brady, Journal of Fluid Mech. **407**, 167 (2000)

9. Dynamics of permeable particles

- Brinkman fluid model
- Applications





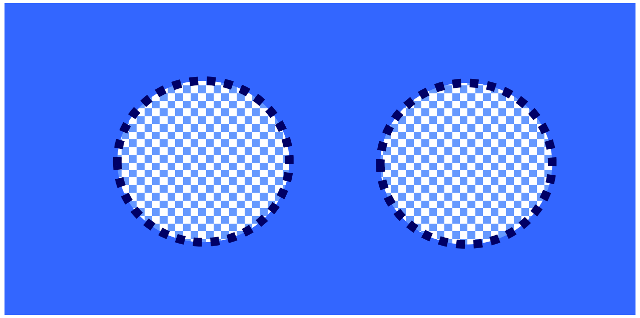
Hydrodynamic model:

- uniformly porous spheres
- rigid skeleton.

Extension to core-shell structure: Abade, Cichocki, Ekiel, Nägele, Wajnryb; J. Chem. Phys. **136**, 104902 (2012)

Microgels: Holmqvist, Mohanty, Nägele, Schurtenberger, Heinen: Phys. Rev. Lett., in press (2012)

9.1 Brinkman fluid model (of porous hard spheres)



$$x = a/\sqrt{k} \sim a/\overline{r}_{pore}$$

inverse fluid penetration depth relative to radius a

Brinkman equation of flow **u** inside a sphere j:

$$\eta_0 \Delta \mathbf{u}(\mathbf{r}) - \nabla p(\mathbf{r}) \underbrace{- (\eta_0 / k)\left[\mathbf{u}(\mathbf{r}) - \mathbf{w}_j(\mathbf{r})\right]} = 0$$

force density due to fluid - skeleton friction

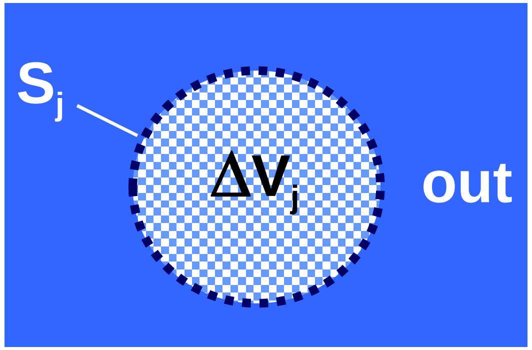
$$\mathbf{w}_j(\mathbf{r}) = \mathbf{V}_j + \mathbf{\Omega}_j \times \left(\mathbf{r} - \mathbf{R}_j\right)$$

small k: zero relative flow (η_0/k) [$\mathbf{u} - \mathbf{w}_j$] ≈ 0 (stick BC)

large k: Stokes flow also inside spheres

- Spheres of uniform porosity k ~ (mean pore size)^2
- Model characterized by: ϕ and inverse penetration depth x
- k depends on size, shape and distribution of interstices (model - dep.)

Boundary conditions and method of calculation



- continuity of **u** on S_j
- continuity of $\boldsymbol{\sigma}$ on S_j

$$\nabla \cdot \sigma_{in}(\mathbf{r}) - (\eta_0 / k)\left[\mathbf{u}(\mathbf{r}) - \mathbf{w}_j(\mathbf{r})\right] = 0$$

Interpretation: induced force density inside S_j

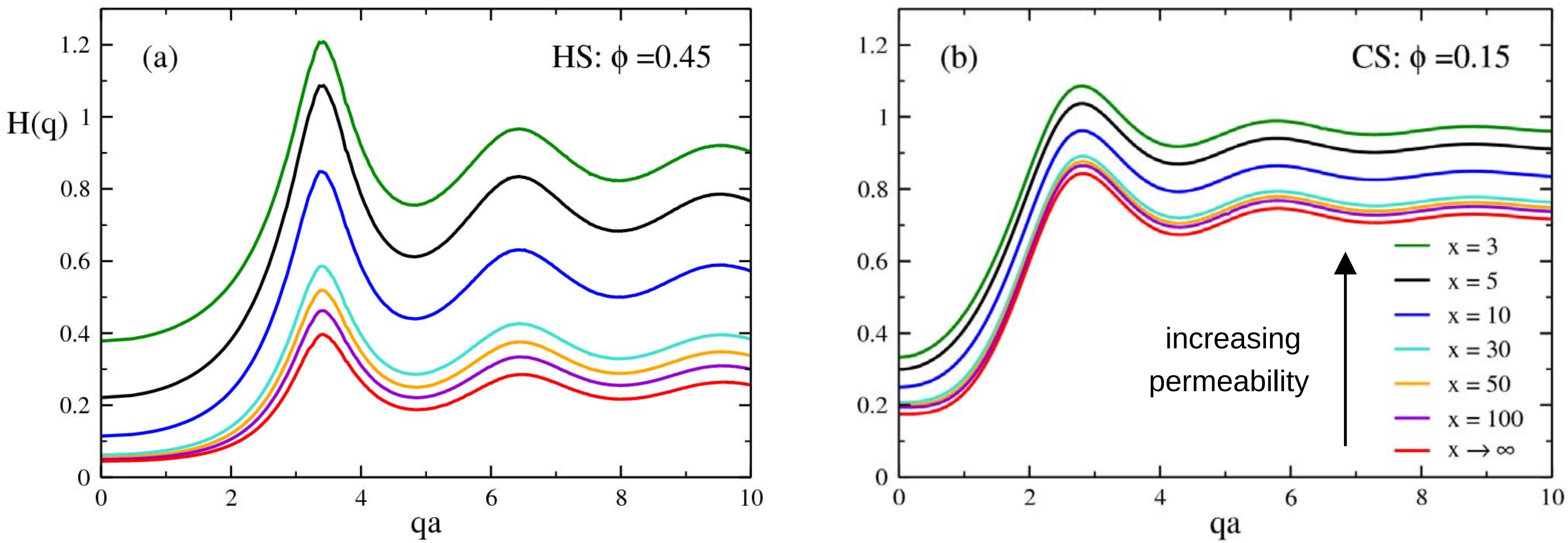
$$\boldsymbol{\sigma}(\mathbf{r}) = -p(\mathbf{r})\mathbf{1} + \eta_0\left[\nabla \mathbf{u}(\mathbf{r}) + \nabla^T \mathbf{u}(\mathbf{r})\right]$$

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

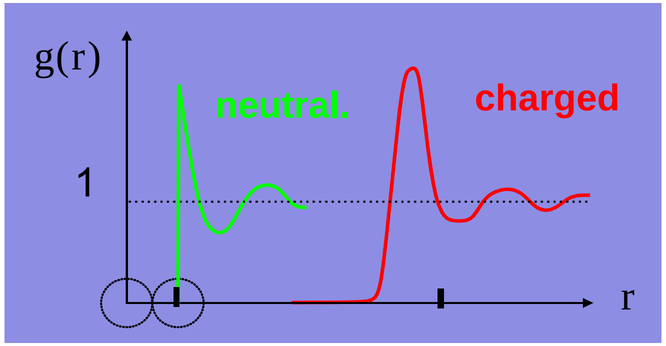
$$\mathbf{F}_j^H = (\eta_0 / k) \int_{\Delta V_j} d\mathbf{r}\left[\mathbf{u}(\mathbf{r}) - \mathbf{w}_j(\mathbf{r})\right] = -\int_{\Delta V_j} d\mathbf{r}\, \mathbf{f}_j(\mathbf{r}) = \int_{S_j} dS\, \boldsymbol{\sigma}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r})$$

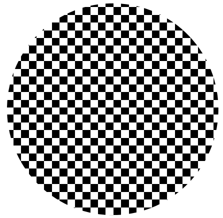
- Use induced force picture (Stokes flow inside & outside spheres)
- Determine many - sphere mobility tensors using spherical multipole expansion method by Cichocki and coworkers (HYDROMULTIPOLE program)

9.2 Applications: Generalized sedimentation coefficient



$$x \approx a / \bar{r}_{pore}$$

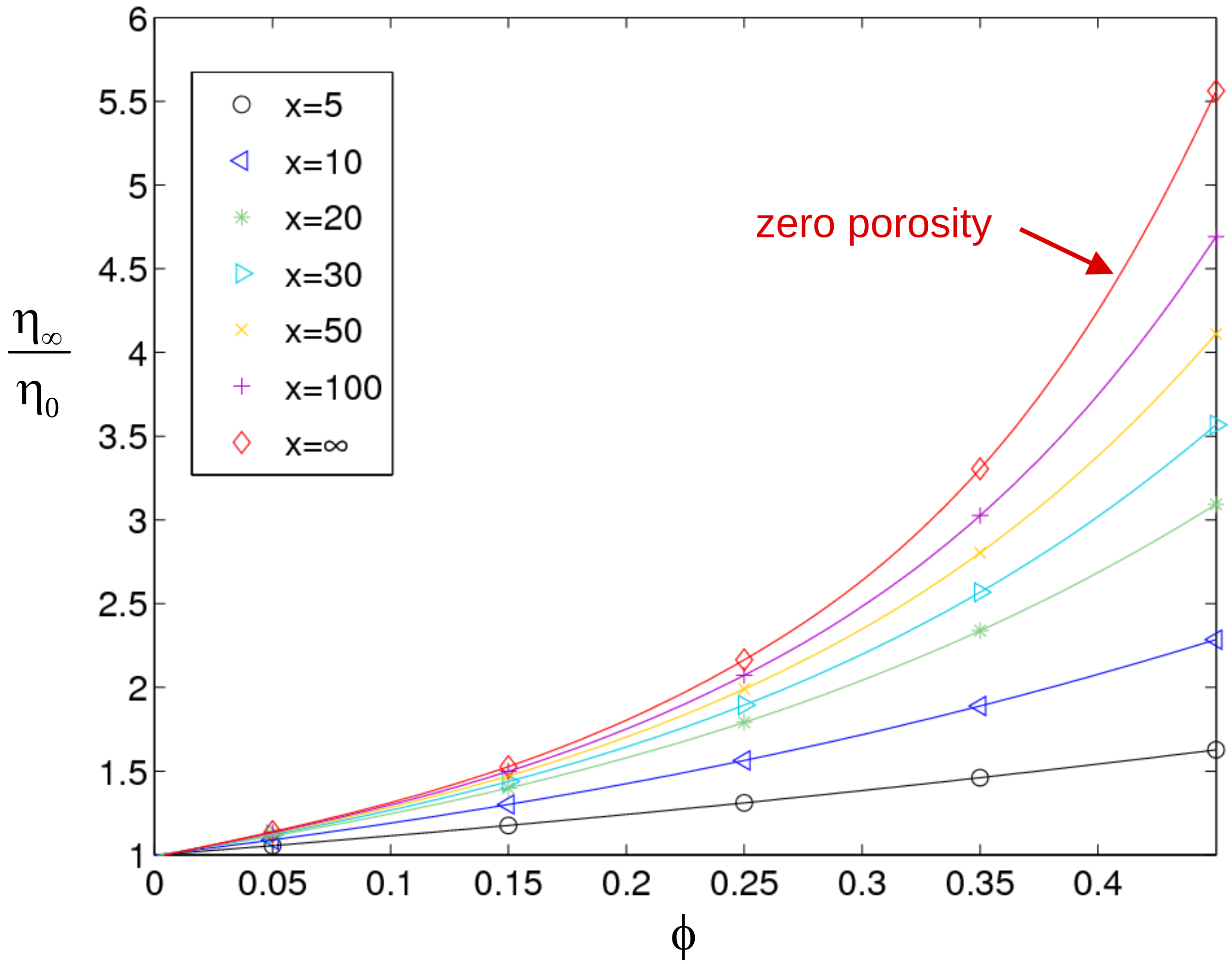




Solvent permeability less influential for charged particles

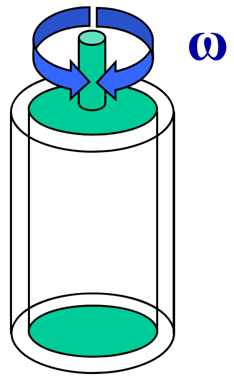
Abade, Cichocki, Ekiel, Nägele, Wajnryb; J. Chem. Phys. **136**, 104902 (2012)

Application: high - frequency viscosity



Abade, Cichocki, Ekiel, Nägele & Wajnryb, JCP **132** (2010) & JPCM **22** (2010)

$$\omega \gg \left(\tau_{\rm diff}\right)^{-1}$$

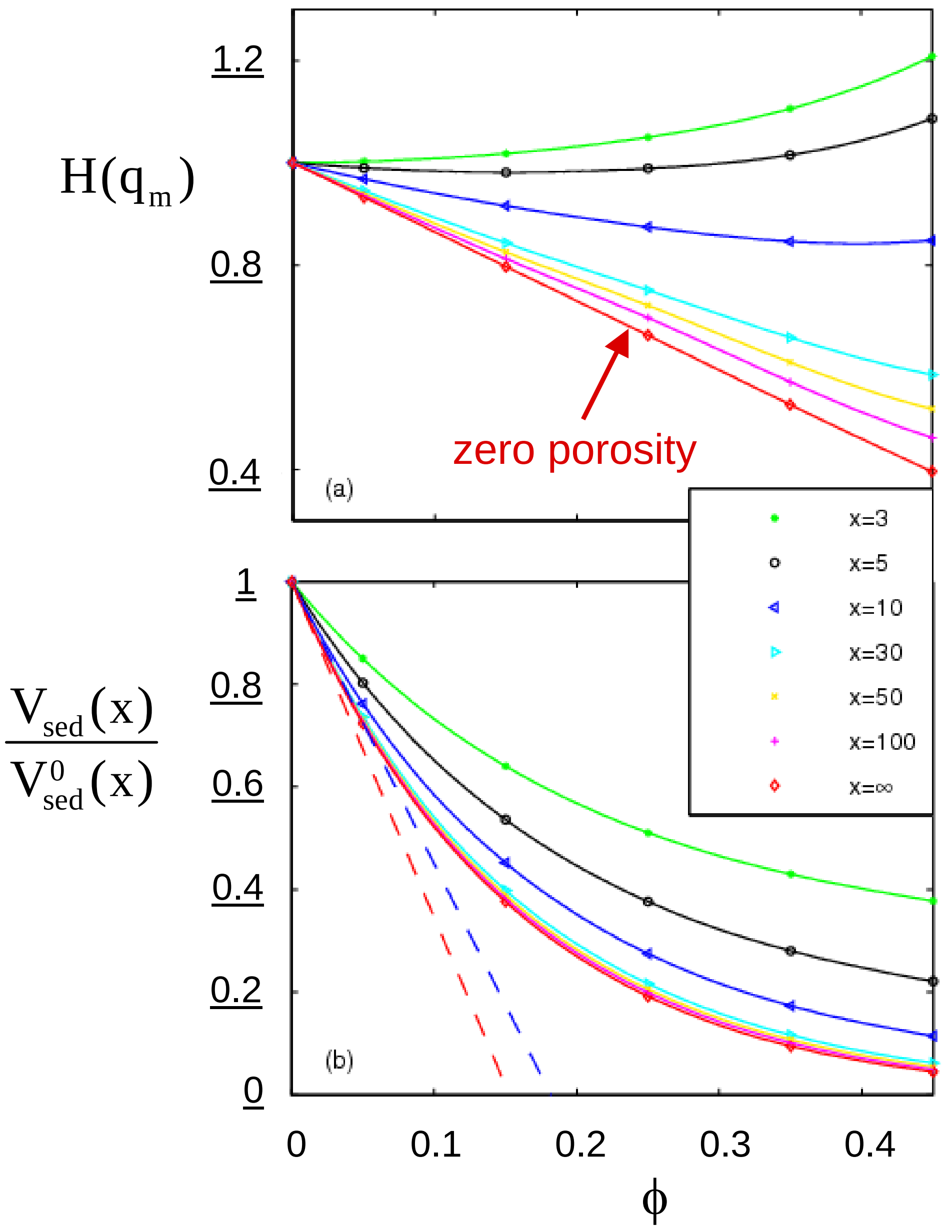


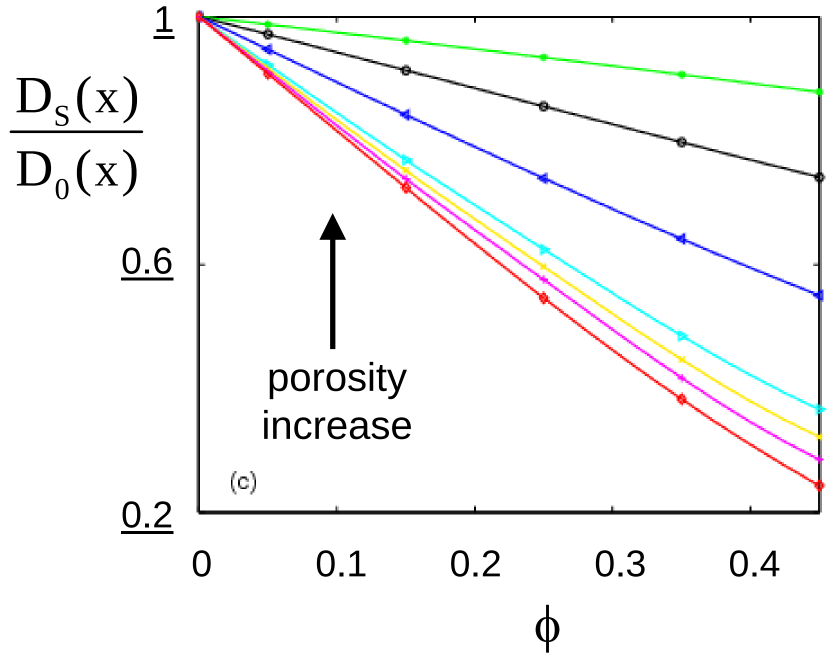
$$\frac{\eta_\infty}{\eta_0} = 1 + [\eta](x)\,\phi + O(\phi^2)$$

$$[\eta] = \begin{cases} 5/2 & (x = \infty) \\ 1 & \text{slip \& bubble} \end{cases}$$

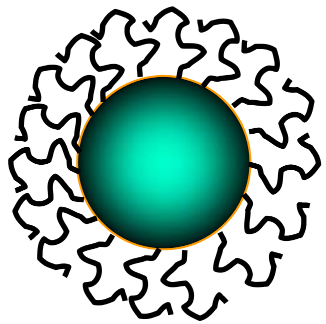
intrinsic viscosity

Short - time properties of porous spheres





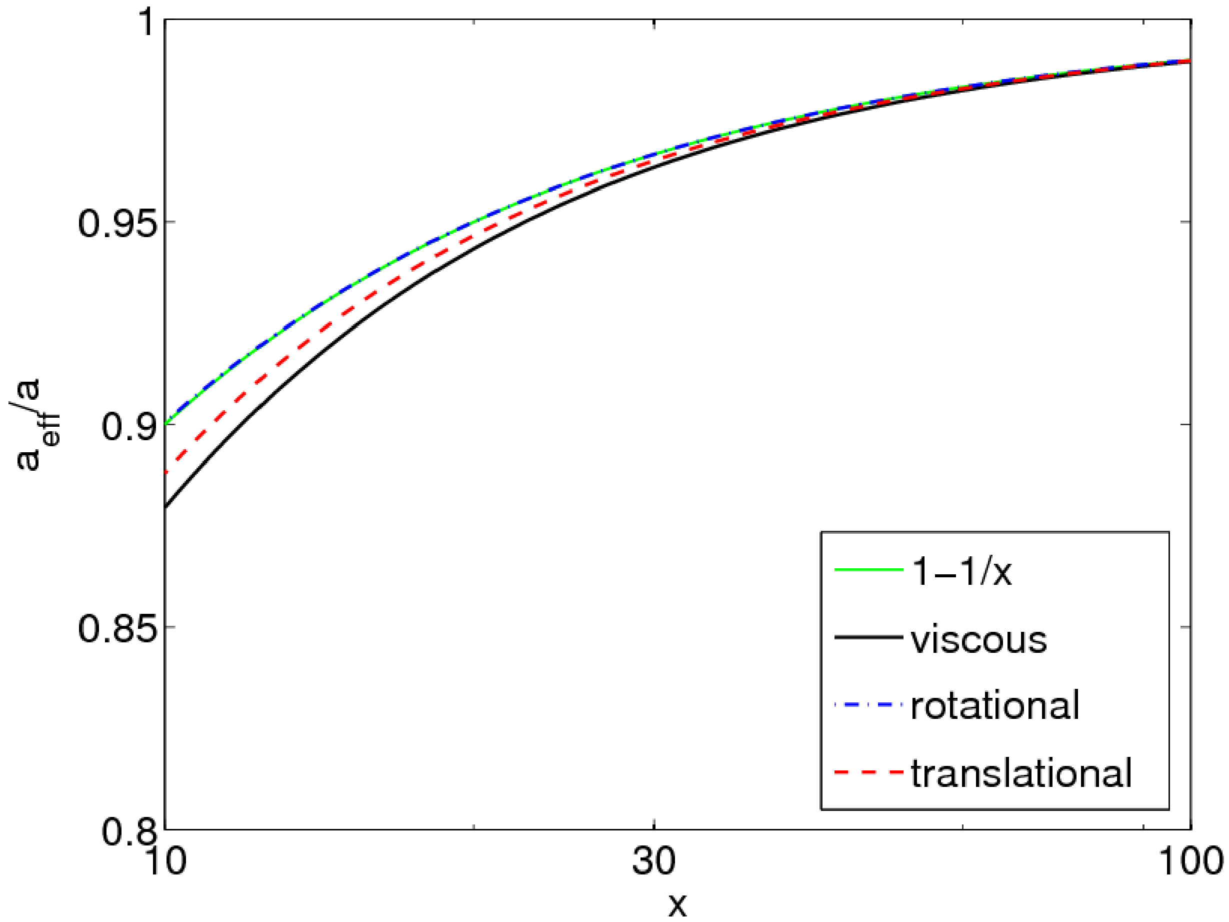
particles with long grafted polymers:



x = 20 - 30

Abade, Cichocki, Ekiel, Nägele, Wajnryb:
JCP **128** (2010) & PRE **81** (2010)

Various definitions of dynamic effective radii



- Effective radii agree practically for x > 30
- Then no distinction between different flow profiles

Abade, Cichocki, Ekiel, Nägele & Wajnryb, JCP **133** (2010)

Generalized Stokes - Einstein (GSE) relations

- translational self-diffusion :

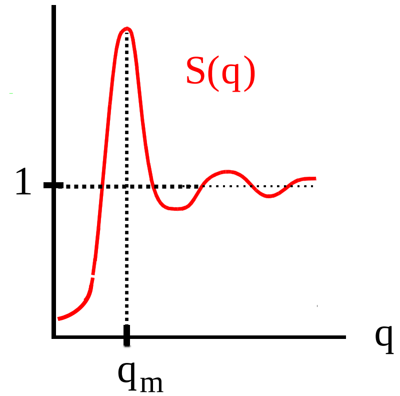
$$D_S(\phi) \overset{?}{\approx} \frac{k_B T}{6\pi\eta_\infty(\phi)a}$$

- rotational self-diffusion :

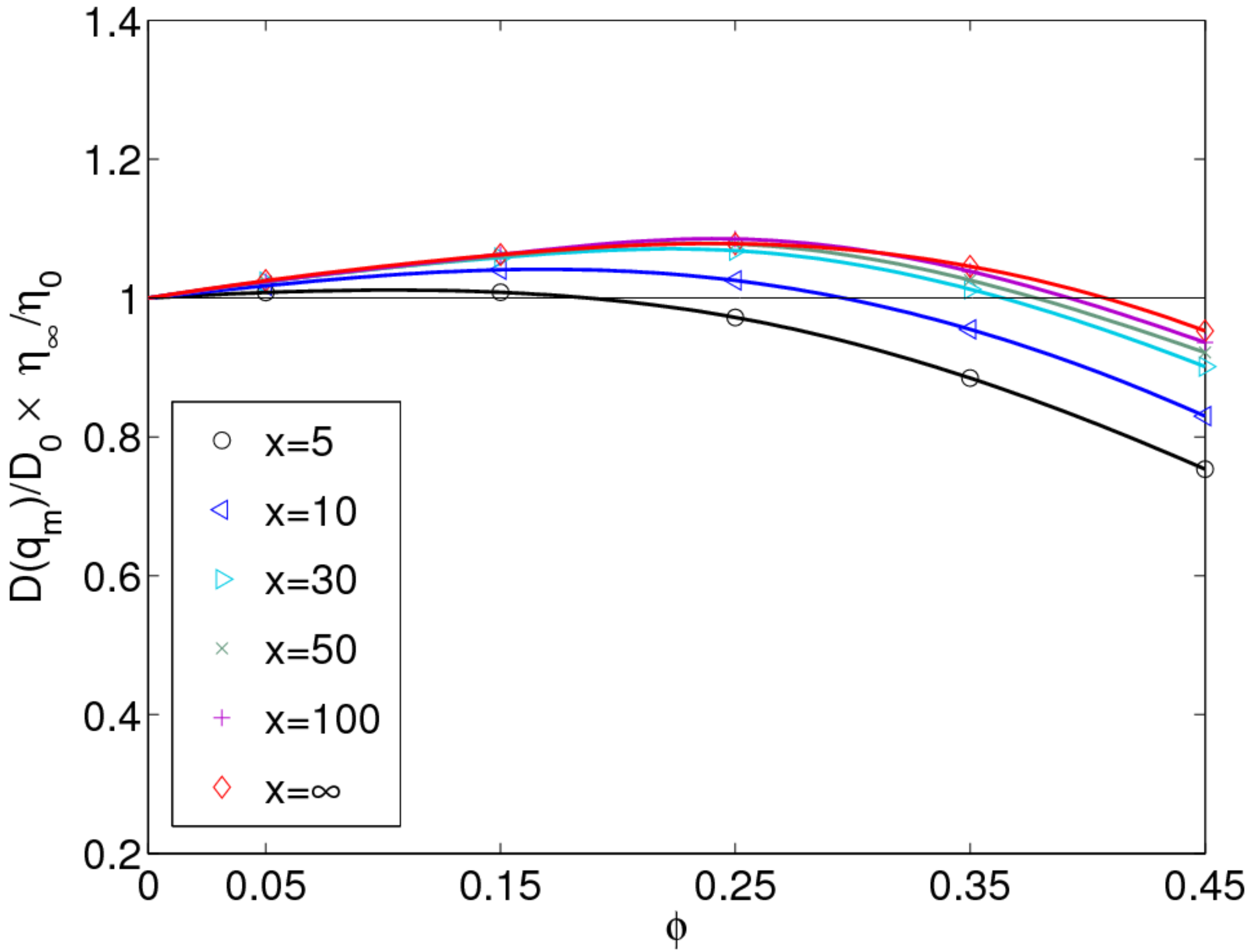
$$D_R(\phi) \overset{?}{\approx} \frac{k_B T}{8\pi\eta_\infty(\phi)a^3}$$

- cage diffusion coefficient:

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

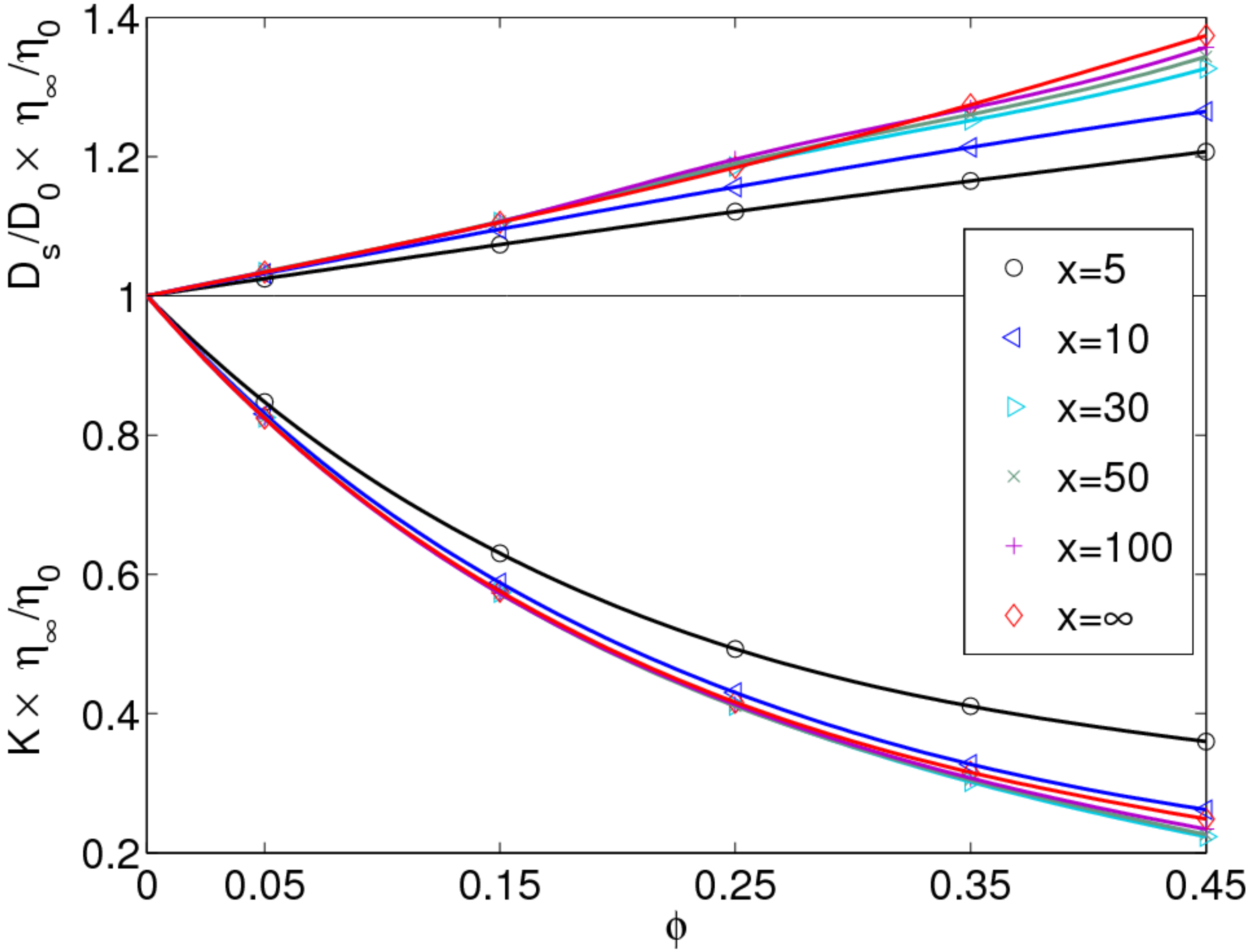


Generalized Stokes-Einstein relations for permeable spheres



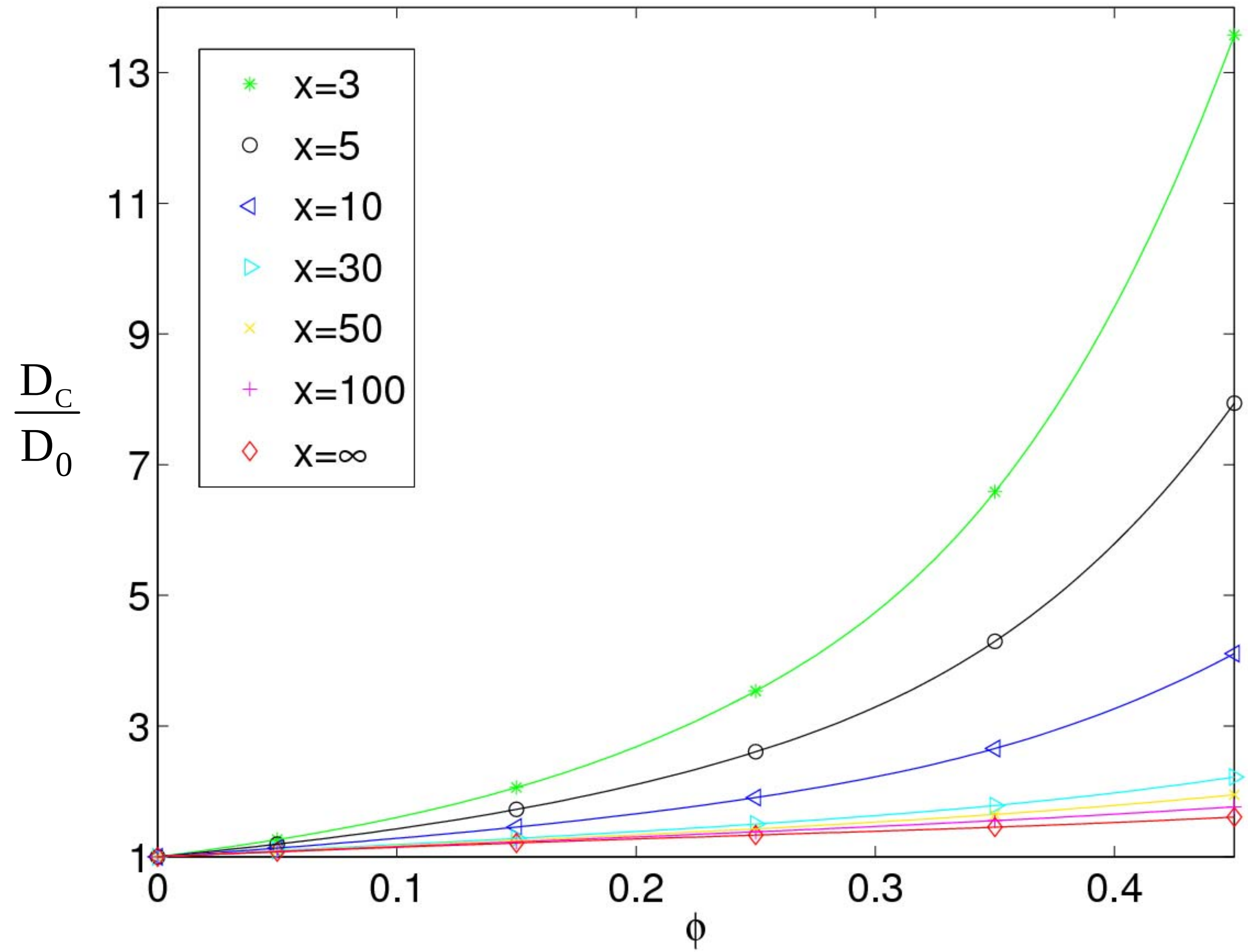
Abade, Cichocki, Ekiel, Nägele & Wajnryb, JPCM **22** (2010)

Test of validity of generalized Stokes-Einstein relations



Abade, Cichocki, Ekiel, Nägele & Wajnryb, JPCM **22** (2010)

Collective diffusion coefficient



10. Appendices

- Derivation of point force solution
- Proof of Mean-Value Theorem
- Multipole method by Chichocki and coworkers

10.1 Derivation of point force solution

- Unbounded infinite fluid::

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

$$\downarrow \qquad\qquad \downarrow$$

$$i\mathbf{q}\, p(\mathbf{q}) - \eta_0 q^2 \mathbf{u}(\mathbf{q}) = -\mathbf{f}(\mathbf{q}) \qquad \mathbf{q} \cdot \mathbf{u}(\mathbf{q}) = \mathbf{0}$$

$$i\mathbf{q} \cdot \mathbf{q}\, p(\mathbf{q}) - \eta_0 q^2 \underbrace{\mathbf{q} \cdot \mathbf{u}(\mathbf{q})}_{=0} = -\mathbf{q} \cdot \mathbf{f}(\mathbf{q}) \quad \Rightarrow$$

$$p(\mathbf{q}) = i \frac{\mathbf{q} \cdot \mathbf{f}(\mathbf{q})}{q^2} \quad \Rightarrow \quad \mathbf{u}(\mathbf{q}) = \frac{1}{\eta_0 q^2} [\mathbf{1} - \hat{\mathbf{q}}\hat{\mathbf{q}}] \cdot \mathbf{f}(\mathbf{q}) \quad \Rightarrow$$ use convolution theorem

$$\mathbf{u}(\mathbf{q}) = \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}}\, \mathbf{u}(\mathbf{r})$$ et cetera

$$\nabla \to -i\mathbf{q}$$

$$\int d\mathbf{q}\, e^{-i\mathbf{q}\cdot\mathbf{r}} A(\mathbf{q}) B(\mathbf{q}) = $$

$$= (2\pi)^3 \int d\mathbf{r}'\, A(\mathbf{r} - \mathbf{r}')\, B(\mathbf{r}')$$

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

$$\mathbf{T}_0(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d\mathbf{q}\, e^{-i\mathbf{q}\cdot\mathbf{r}} \frac{1}{\eta_0 q^2} [\mathbf{1} - \hat{\mathbf{q}}\hat{\mathbf{q}}] = \frac{1}{8\pi\eta_0 r} [\mathbf{1} + \hat{\mathbf{r}}\hat{\mathbf{r}}]$$

$$\mathbf{Q}_0(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d\mathbf{q}\; e^{-i\mathbf{q}\cdot\mathbf{r}} \left(i \frac{\mathbf{q}}{q^2} \right) = \frac{-1}{(2\pi)^3} \nabla_r \int d\mathbf{q}\; e^{-i\mathbf{q}\cdot\mathbf{r}} \frac{1}{q^2} = \frac{1}{4\pi r^3} \mathbf{r}$$

- have employed that :

$$\int d\mathbf{q} = \int_0^\infty dq\, q^2 \int_{4\pi} d\Omega_q$$

$$\int d\Omega_q\, e^{\pm i\mathbf{q}\cdot\mathbf{r}}\, \mathbf{1} = 4\pi\, j_0(q\,r)\,\mathbf{1}$$

$$\int d\Omega_q\, e^{\pm i\mathbf{q}\cdot\mathbf{r}}\, \hat{\mathbf{q}}\,\hat{\mathbf{q}} = 4\pi\left[\frac{j_1(q\,r)}{q\,r}\mathbf{1} - j_2(q\,r)\,\hat{\mathbf{r}}\,\hat{\mathbf{r}}\right]$$

$$j_2(x) = \frac{3\,j_1(x)}{x} - j_0(x)$$

10.2 Proof of mean - value theorem

- Expand around center of sphere i:

$$\mathbf{u}_\infty(\mathbf{r}) = \sum_{n=0}^{\infty} \frac{(\mathbf{r}-\mathbf{R}_i)^n \odot \nabla^n}{n!} \mathbf{u}_\infty(\mathbf{r})\Big|_{\mathbf{r}=\mathbf{R}_i} = \mathbf{u}_\infty(\mathbf{R}_i) + (\mathbf{r}-\mathbf{R}_i)\cdot\nabla\mathbf{u}_\infty(\mathbf{R}_i) + \frac{1}{2}(\mathbf{r}-\mathbf{R}_i)(\mathbf{r}-\mathbf{R}_i):\nabla\nabla\mathbf{u}_\infty(\mathbf{R}_i) + ..$$

$$\nabla^2\nabla^2\mathbf{u}_\infty = 0 \qquad \nabla\cdot\mathbf{u}_\infty = 0$$

$$\int_{x=a} dS \underbrace{\mathbf{x}\ldots\mathbf{x}\,\mathbf{x}}_{\text{odd factors}} = 0$$ since odd integrands $(\mathbf{x} = \mathbf{r} - \mathbf{R}_i)$

⇨

$$\int_{S_i} dS\, \mathbf{u}_\infty(\mathbf{r}) = 4\pi a^2 \mathbf{u}_\infty(\mathbf{R}_i) + 0 + \underbrace{\left(\frac{1}{2}\int_{S_i} dS\,\mathbf{x}\,\mathbf{x}\right)}_{\frac{4\pi}{6}a^4\mathbf{1}} : \nabla\nabla\mathbf{u}_\infty(\mathbf{R}_i) + 0$$

$$\int_{S_i} dS\, \mathbf{u}_\infty(\mathbf{r}) = 4\pi a^2 \left(\mathbf{1} + \frac{a^2}{6}\nabla^2\right)\mathbf{u}_\infty(\mathbf{R}_i)$$

Generalizations: R. Courant and D. Hilbert, *Introduction to Mathematical Physics II*, Springer (1968).

10. 3 Symmetry of mobility and friction matrices

- Consider two solutions ($\mathbf{u}_A$, p_A, $\mathbf{f}_A$) and ($\mathbf{u}_B$, p_B, $\mathbf{f}_B$) of Stokes equation (linearity!)

$$\nabla \cdot \left[\boldsymbol{\sigma}_A \cdot \mathbf{u}_B - \boldsymbol{\sigma}_B \cdot \mathbf{u}_A \right] = \mathbf{f}_B \cdot \mathbf{u}_A - \mathbf{f}_A \cdot \mathbf{u}_B$$

Lorentz reciprocity relation

- Use for A and B the N - sphere BVP with stick BC in quiescent fluid ($\mathbf{u}$ = 0 at ∞)
- Integrate over all space (super - vector notation):

$$0 = \int d\mathbf{r} \, \nabla \cdot [\ldots] = \left(F_B \cdot V_A - F_A \cdot V_B \right) + \left(T_B \cdot \Omega_A - T_A \cdot \Omega_B \right)$$

$$\mathbf{F}_i = \int_{\Delta V_i^+} d\mathbf{r} \, \mathbf{f}_i$$

$$\mathbf{T}_i = \int_{\Delta V_i^+} d\mathbf{r} \left(\mathbf{r} - \mathbf{R}_i \right) \times \mathbf{f}_i$$

$V_A = \mu^{tt} \cdot F_A$ & $V_B = \mu^{tt} \cdot F_B$ when $T_A = 0 = T_B$

$\rightarrow$ $F_B \cdot \mu^{tt} \cdot F_A = F_A \cdot \mu^{tt} \cdot F_B$ $\rightarrow$ $\mu^{tt} = \left(\mu^{tt} \right)^{Tr}$

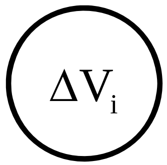
- More generally since forces and torques can be selected arbitrarily:

$$\begin{pmatrix} \mu^{tt} & \mu^{tr} \\ \mu^{rt} & \mu^{rr} \end{pmatrix} = \begin{pmatrix} \mu^{tt} & \mu^{tr} \\ \mu^{rt} & \mu^{rr} \end{pmatrix}^{Tr} \rightarrow \begin{pmatrix} \zeta^{tt} & \zeta^{tr} \\ \zeta^{rt} & \zeta^{rr} \end{pmatrix} = \begin{pmatrix} \zeta^{tt} & \zeta^{tr} \\ \zeta^{rt} & \zeta^{rr} \end{pmatrix}^{Tr}$$

10.4 Multipole method by Cichocki and coworkers

- N spheres with stick BC in unbound fluid with ambient flow $\mathbf{u}_0(r)$

$$\mathbf{w}_i(\mathbf{r}) = \mathbf{V}_i + \mathbf{\Omega}_i \times \left(\mathbf{r} - \mathbf{R}_i\right)$$



For **r** inside and on sphere i: $\mathbf{r} \in \Delta V_i$

$$\mathbf{w}_i(\mathbf{r}) = \mathbf{u}_0(\mathbf{r}) + \int d\mathbf{r}'\, \mathbf{T}_0(\mathbf{r},\mathbf{r}') \cdot \mathbf{f}_i(\mathbf{r}') + \sum_{j \neq i}^{N} \int d\mathbf{r}'\, \mathbf{T}_0(\mathbf{r},\mathbf{r}') \cdot \mathbf{f}_j(\mathbf{r}')$$

localized on surface S_j

(for stick & slip-stick BC)

Define Green integral operator (propagator) G(ij) for $i \neq j$ by

$$\left(\mathbf{G}(ij)\mathbf{f}_j\right)(\mathbf{r}) = \int d\mathbf{r}'\, \mathbf{T}_0(\mathbf{r},\mathbf{r}') \cdot \mathbf{f}_j(\mathbf{r}') \qquad \left(\mathbf{r} \in \Delta V_i^{+}\right)$$

G(ij) depends on **solvent properties** & outer BC only (here Oseen tensor)

Incident flow inside sphere i volume (non - singular therein):

$$\mathbf{u}_{inc}(\mathbf{r}) = \mathbf{u}_0(\mathbf{r}) + \sum_{j \neq i}^{N} \left(\mathbf{G}(ij)\mathbf{f}_j\right)(\mathbf{r})$$

By linearity of Stokes flow is:

$$\mathbf{f}_i(\mathbf{r};X) = \int d\mathbf{r}'\, \zeta_0(\mathbf{r},\mathbf{r}') \cdot [\mathbf{w}_i(\mathbf{r}';X) - \mathbf{u}_{inc}(\mathbf{r}';X)]$$

Single – sphere friction kernel ζ_0 (localized on S_i) depends on hydrodynamic model & BC of a single sphere only, and not on X

Use again short – hand notation by omitting field variables and integral w / r **r**´:

$$\mathbf{f}_i = \mathbf{Z}_0(i)[\mathbf{w}_i - \mathbf{u}_{inc}] \qquad (\mathbf{Z}_0 \Leftrightarrow \zeta_0(\mathbf{r},\mathbf{r}'))$$

Single - sphere friction operator has obviously an inverse: $\mathbf{w}_i - \mathbf{u}_{inc} = \mathbf{Z}_0^{-1}(i)\mathbf{f}_i$

Insertion of incident flow gives:

$$\mathbf{w}_i - \mathbf{u}_0 = \mathbf{Z}_0^{-1}(i)\,\mathbf{f}_i + \sum_{j \neq i}^{N} \mathbf{G}(i\,j)\,\mathbf{f}_j$$

integral equations for induced force densities

Introduce super – vector / matrix notation: $w - u_0 = (\mathbf{w}_1 - \mathbf{u}_0, \ldots, \mathbf{w}_N - \mathbf{u}_0)$ et cetera

$$\hat{G} \Leftrightarrow \sum_j (1 - \delta_{ij})\, \mathbf{G}(ij)$$

$$\hat{Z}_0^{-1} \Leftrightarrow \sum_j \delta_{ij}\, \mathbf{Z}_0^{-1}(i)$$

Allows to write integral equations more compactly as:

$$w - u_0 = \hat{Z}_0^{-1} f + \hat{G} f = \left(\hat{Z}_0^{-1} + \hat{G}\right) f$$

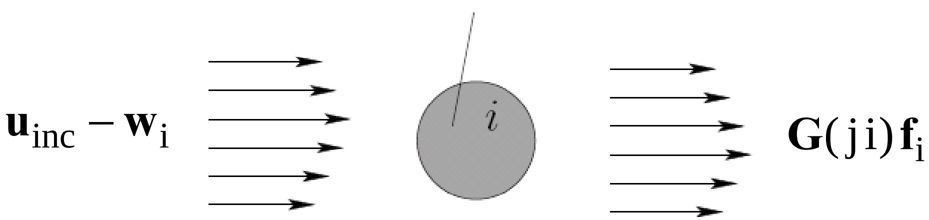
Again inversion is allowed because of 1-1 correspondence:

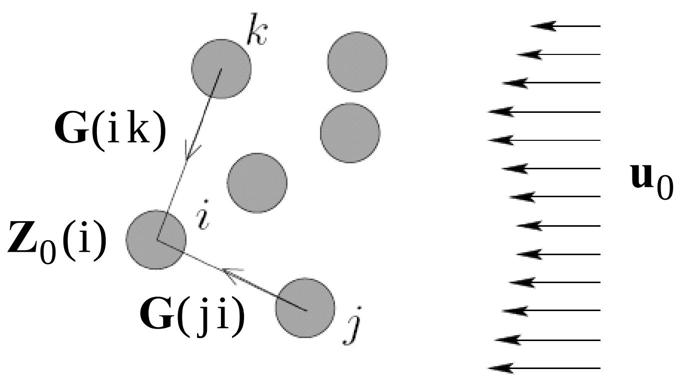
$$f = \left[\hat{Z}_0^{-1} + \hat{G}\right]^{-1} (w - u_0) = \hat{Z}_0 \left[1 + \hat{G}\,\hat{Z}_0\right]^{-1} (w - u_0)$$ (formal solution for f)

Formally expand in multiple scattering series (friction problem):

$$\boxed{f = \hat{Z}_0 \left[1 - \hat{G}\,\hat{Z}_0 + \hat{G}\,\hat{Z}_0 \hat{G}\,\hat{Z}_0 - \ldots\right] (w - u_0)}$$

$$\mathbf{f}_i = \mathbf{Z}_0(i)\left[\mathbf{w}_i - \mathbf{u}_{inc}\right]$$





- Obtain coresponding multiple scattering series for mobility problem
- Project on basic set of spherical tensor multipoles $\left(|ilm\sigma\rangle,\ \sigma = 0,1 \right)$
- Infinite set of linear algebraic equations relating spherical force and velocity multipoles
- Truncate set at multipolar order L $(L \geq 3)$
- Lubrication correction: modified version of method by Durlofsky, Brady and Bossis
- Positive definiteness and symmetry of exact mobility matrix is preserved
- Advantage: only $\mathbf{Z}_0$ must be changed when changing particle model

B. Cichocki et al., J. Chem. Phys. **112** (2000)

L. Durlofsky, J.F. Brady, and G. Bossis, J. Fluid Mech. **180** (1987)

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