# Dynamics of Dispersion Colloids

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# Overview

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2. **Salient static properties**
3. **Dynamic light scattering**
4. **Theoretical description of colloid dynamics**
5. **Hydrodynamic mobility problem of many spheres**
6. **Basic properties of Smoluchowski dynamics**
7. **Short-time dynamics**
8. **Long-time dynamics**
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    - Modell dispersions and direct particle forces
    - Hydrodynamic interaction (HI)
    - Dynamics on colloidal time scales
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    - Static light scattering and structure factor
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8. **Long-time dynamics**
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    - Mode coupling approximation of memory functions
    - Application: non-exponential decay of dynamic structure factor
9. **Concluding remarks**

# General literature

1. W.B. Russel, D.A. Saville, and W.R. Schowalter, *Colloidal Dispersions* (Cambrigde University Press, 1989)
2. J.K.G. Dhont, *An Introduction to Dynamics of Colloids* ( Elsevier, Amsterdam, 1996)
3. R. Pecora, *Dynamic Light Scattering*, (Plenum Press, New York, 1985)
4. G. Nägele, *The Physics of Colloid Soft Matter: Lecture Notes 14* (Polish Academy of Sciences Publishing, Warsaw, 2004)
5. G. Nägele, *On The Dynamics and Structure of Charge-Stabilized Colloidal Suspensions* (Physics Reports 272, pp. 215-372, 1996)
6. R.M. Mazo, *Brownian Motion: Fluctuations, Dynamics and Applications* (Clarendon Press, Oxford, 2002)
7. R. Zwanzig, *Non-Equilibrium Statistical Mechanics* (Oxford University Press, 2001)

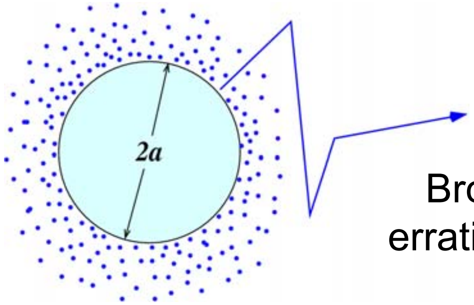
# 1. Introduction & motivation

- **Examples of colloidal dispersions**
- **Modell dispersions and direct particle forces**
- **Hydrodynamic interaction (HI)**
- **Dynamics on colloidal times scales**

# Examples of colloidal dispersions

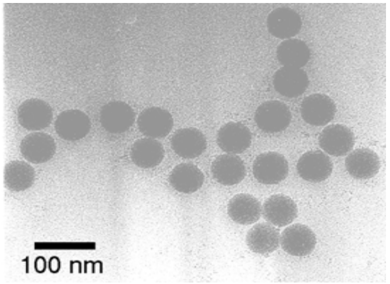
**Definition:** 1 nm < $\varnothing$ < 10 $\mu$m

**Examples:**
micellar systems
microemulsions
proteins
viruses
inorganic particles
(goldsol, Silica, ...)



Brownian
erratic motion

Solvent: $H_2O$, ...



**Industrial products:**
dispersion paints
pharmaceuticals
food stuff
cosmetics
waste water

**Theoretical task:**

- Particle properties/interactions

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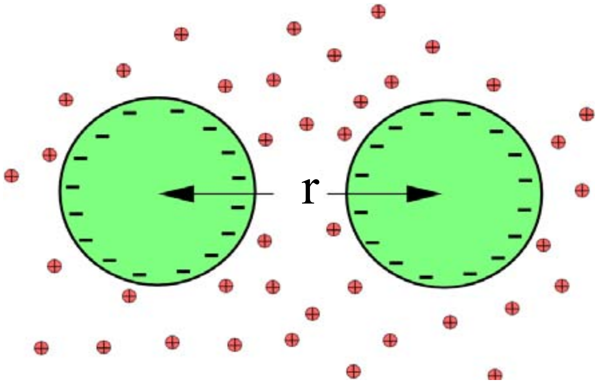
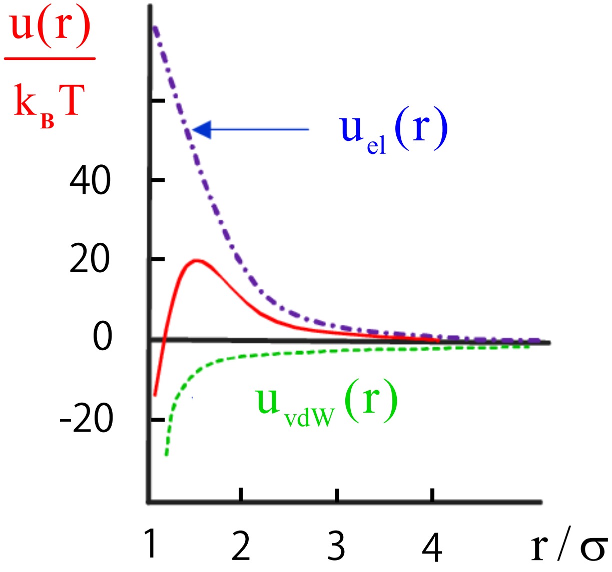
- Transport properties:
  - diffusion coefficients
  - viscosities
  - conductivities

# Model dispersions in 3D

## Charge-stabilized dispersions :

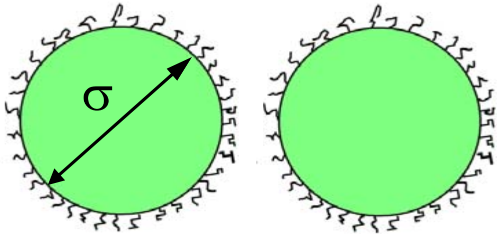


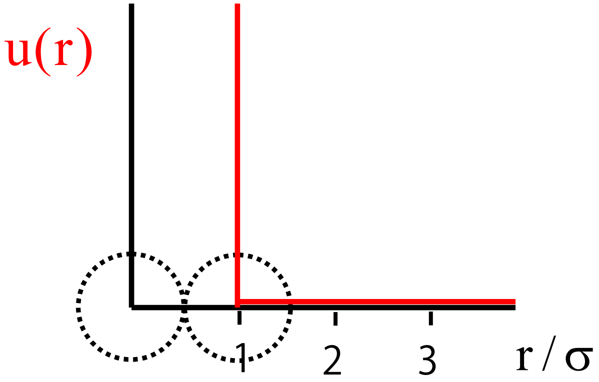
$$u_{el}(r) \propto Q^2 \exp\{-\kappa r\}/r \quad , \quad r > \sigma$$



$$u(r) \approx u_{el}(r) \text{ für } Q/e >> 1$$

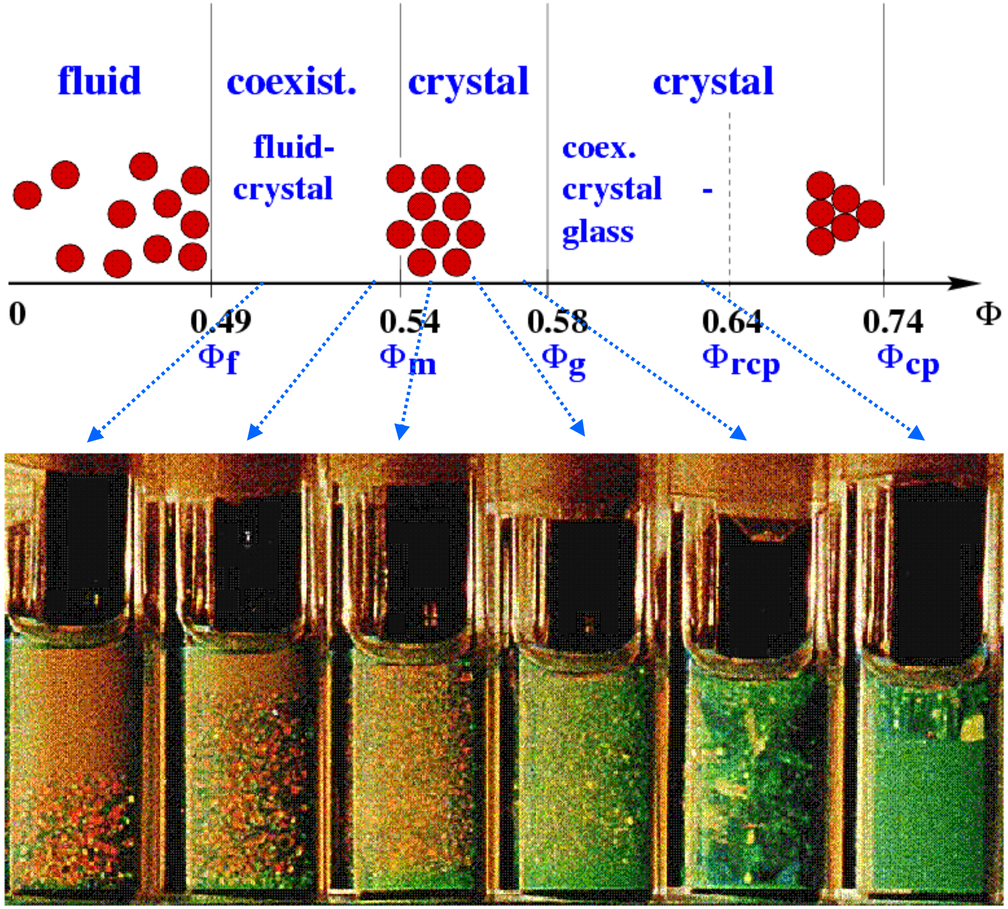
## Sterically stabilized dispersions :





- Range and strength of $u(r)$ is tunable

# Phase behavior of colloidal hard-sphere dispersion

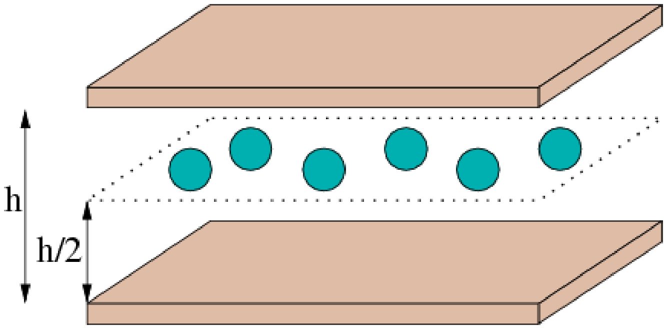


Pusey & van Megen
Nature 320, 1986

- Present lectures restricted on colloidal systems in fluid one-phase region

# Quasi-two-dimensional model dispersions

**Colloidal spheres between two walls**

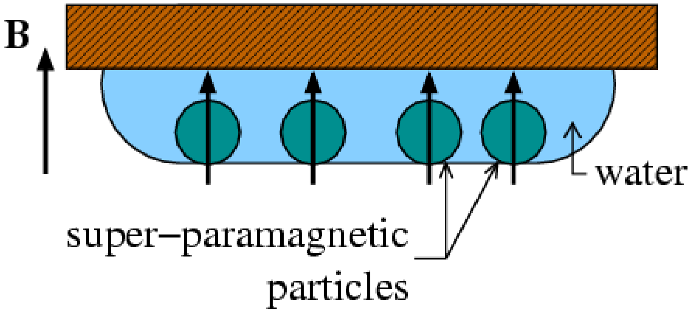


$$u(r) = \begin{cases} \infty\,, & r < \sigma \\ Q^2 \dfrac{e^{-\kappa r}}{\varepsilon r}\,, & r > \sigma \quad \left(\kappa = \dfrac{\pi}{h\sqrt{2}}\right) \end{cases}$$

- Yukawa-type model potential

  (Chang & Hone, EPL 5, ´88)

**Magnetic spheres at water-air interface**



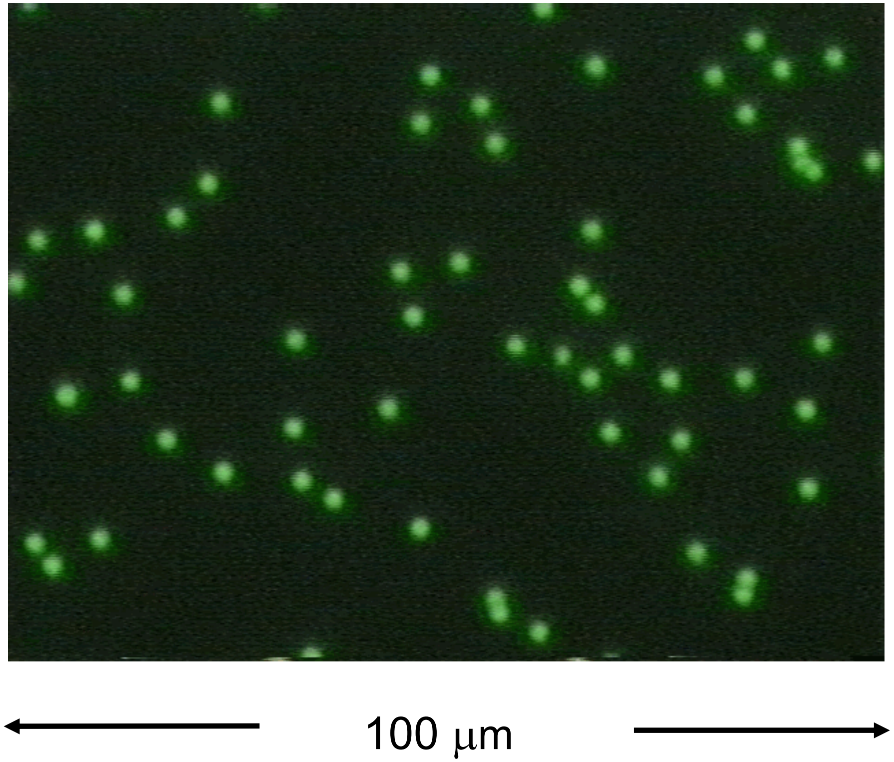
$$u(r) = \frac{\mu_0 \chi_{\mathrm{eff}}^2}{4\pi} \frac{B^2}{r^3}$$

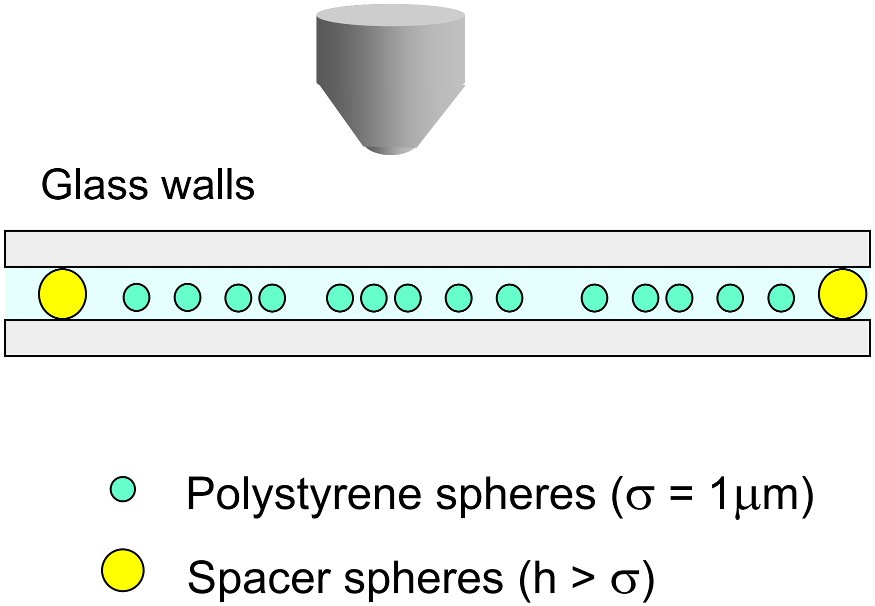
- Well-characterized dipolar potential

  (Zahn & Maret, PRL 85, ´00)

# Experimental realization: Brownian forces

Courtesy: J.L. Arauz-Lara, Univ. of San Luis Potosi





Video microscopy

Glass walls

● Polystyrene spheres ($\sigma$ = 1μm)

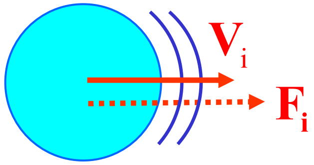
● Spacer spheres (h > $\sigma$)

**Colloidal particle dynamics determined by interplay of:**

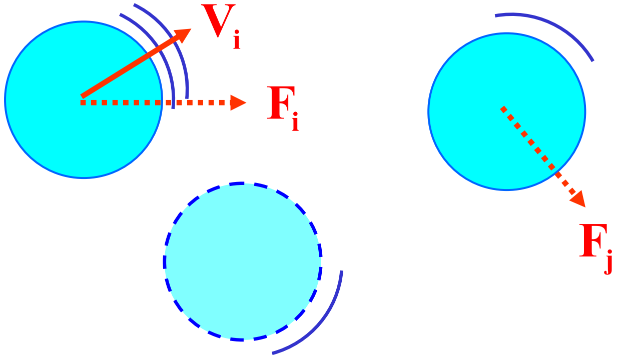
1. Direct particle interactions (DI)
2. Brownian erratic forces due to solvent molecules‘ bombardement
3. Hydrodynamic interactions through solvent (HI)

# Hydrodynamic interaction (HI)

- Long-range dynamic many-body force $\sim \mathrm{r}^{-1}$
- Quasi-instantaneous & inertia-free on colloidal time scales
- Small-Reynolds-number creeping solvent flow



$$\mathbf{v}_\mathbf{i} = \frac{\mathrm{D}_0}{\mathrm{k_B T}}\mathbf{F}_\mathbf{i} \qquad \mathrm{D}_0 = \frac{\mathrm{k_B T}}{6\pi\eta_0 \mathrm{a}}$$

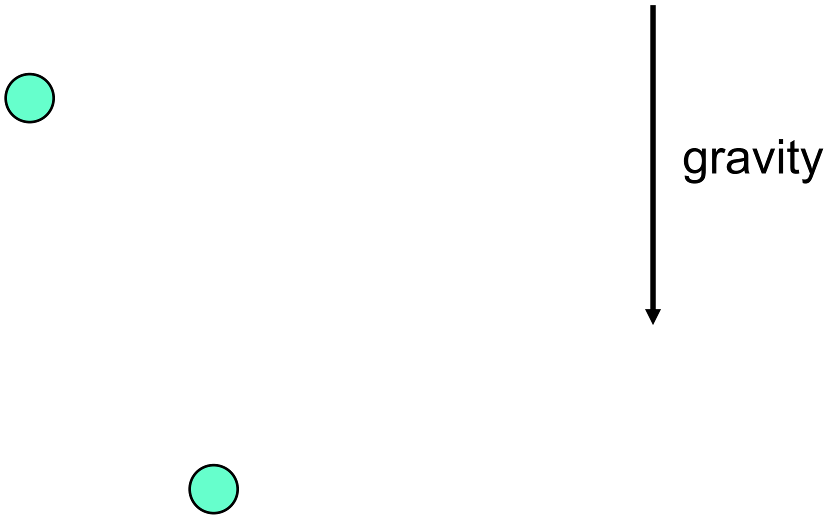


$$\boxed{\mathbf{v}_\mathbf{i} = \frac{1}{\mathrm{k_B T}}\sum_{\mathbf{j}=1}^{\mathrm{N}} \mathbf{D}_{\mathbf{ij}}(\mathbf{r}^{\mathrm{N}})\cdot\mathbf{F}_\mathbf{j}}$$

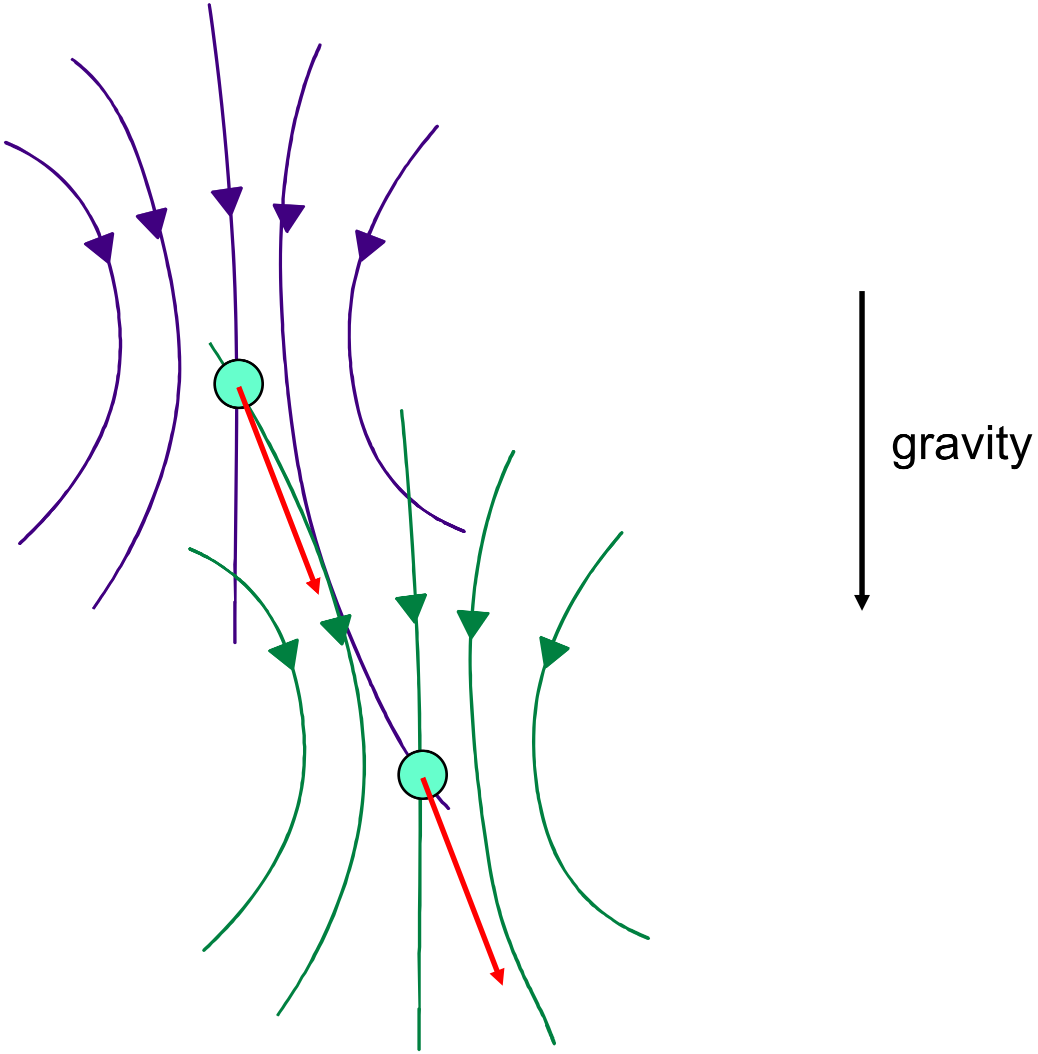
hydrodynamic mobility tensor (non-linear in $\mathbf{r}^{\mathrm{N}}$)

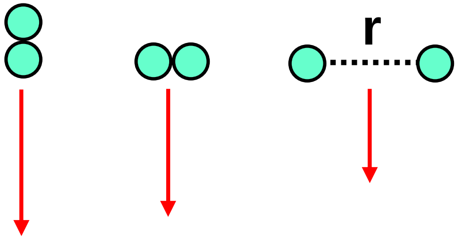
( generalized Stokes‘ friction law )

# HI: Non-Brownian sedimentation of two small spheres



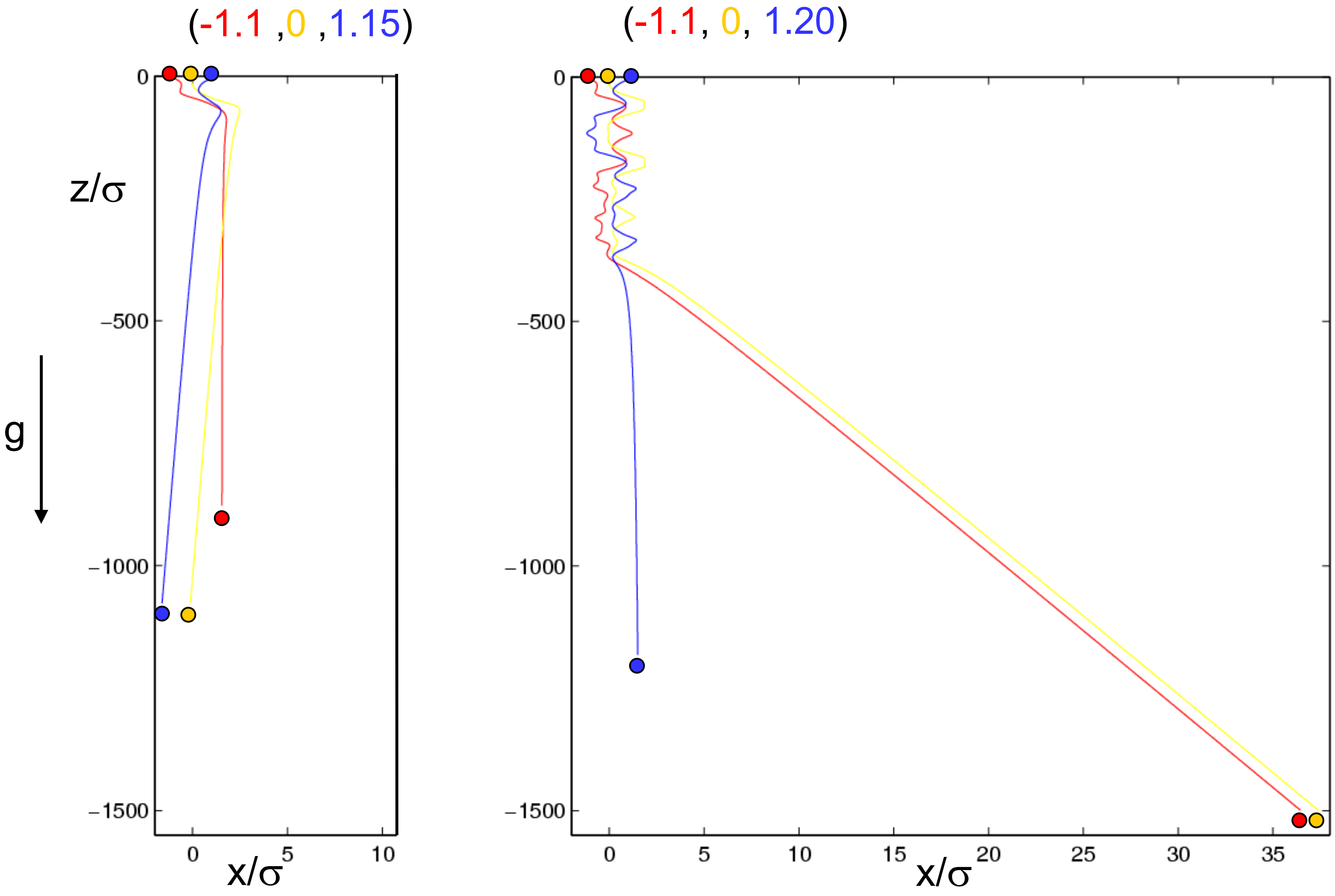
# HI: Non-Brownian sedimentation of two small spheres





- fixed distance vector **r**

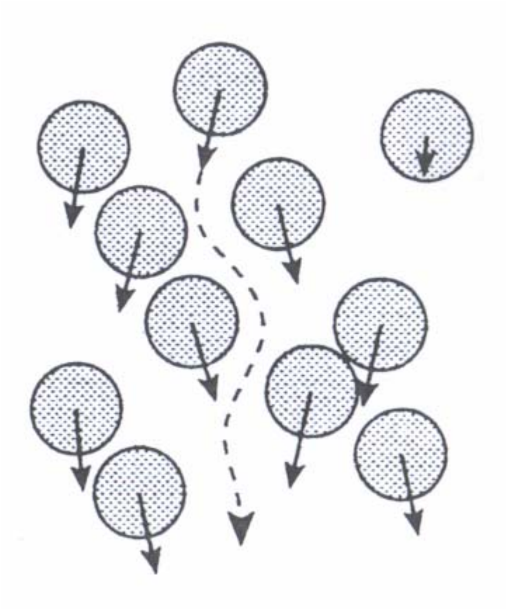
# Asymmetric initial configuration of three spheres at z = 0

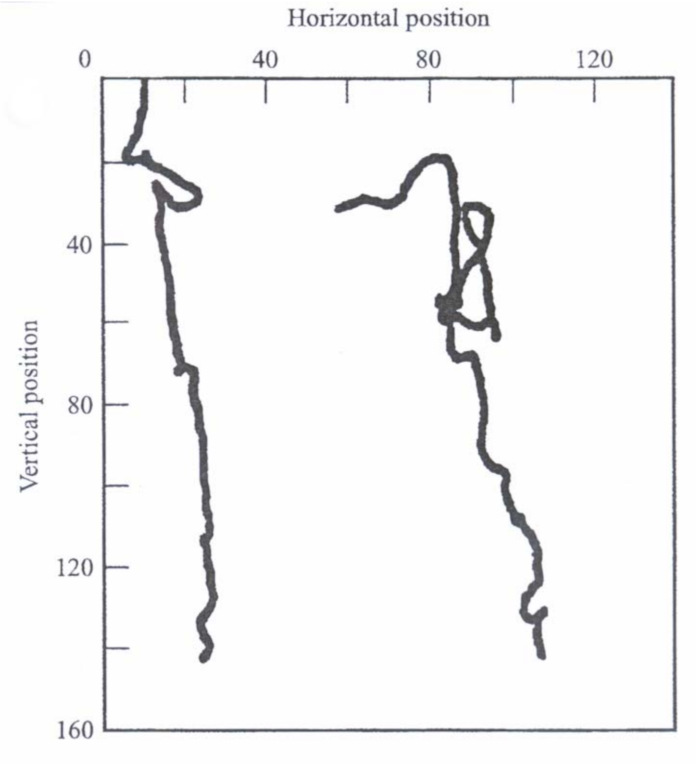


- Sensitive dependence on initial configuration for N > 2 → chaotic trajectories

Courtesy : M. Ekiel-Jezewska and E. Waijnryb (unpublished results, 2004)

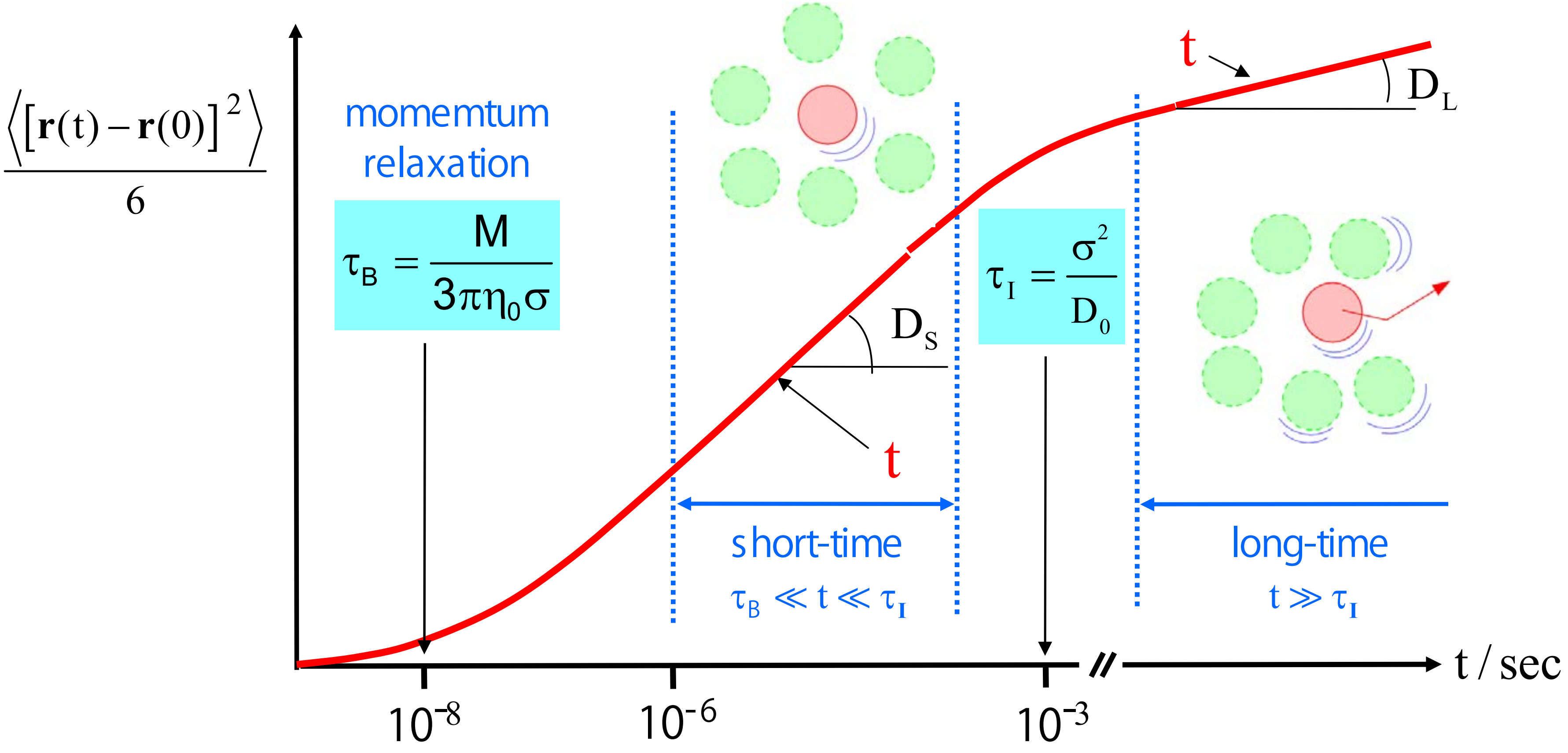
# HI: Non-Brownian sedimentation of many spheres





- meandering trajectories & fluctuating velocities
- hydrodynamic „diffusion“ due to HI
- existence & form of final stationary particle distribution $P_{stat}(\mathbf{r}^N)$ still under debate
- slowly sedimenting colloidal particles → Brownian trajectories, $P_{stat}(\mathbf{r}^N)$ existent

# Dynamics on colloidal time scales



DLS $t \gg \tau_B$: overdamped Langevin-Eq.

generalized Smoluchowski-Eq.

# Dynamics on colloidal time scales

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

$$\Delta t >> \tau_B \approx 10^{-8} \text{ sec}$$

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

“stopping distance”

Rhodospirillum bacteria (length $\sigma \approx 5\ \mu m$)

# Dynamics on colloidal time scales

Overdamped Langevin-Eq.

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

Random force
(solvent collisions)

Dynamic simulations

Generalized Smoluchowski Eq.

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

PDF

coarse-grained velocity from
force balance

Theoretical calculations

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

# 2. Salient static properties

- **Pair distribution function**
- **Static light scattering and structure factor**
- **Methods of calculation**

# Pair distribution function

Canonical NVT-ensemble:  N >> 1 spherical particles in volume V at temperature T

$$\rho_N^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = \underbrace{N(N-1)\ldots(N-n+1)}_{\text{n out of N}} = \int d\mathbf{r}_{n+1}\ldots d\mathbf{r}_N \underbrace{\frac{e^{-\beta U(\mathbf{r}^N)}}{Z_N}}_{\text{probability d.f. of } r^N}$$

joint d.f. for n << N particles at $\{\mathbf{r}_1,\ldots,\mathbf{r}_n\} = \mathbf{r}^n$

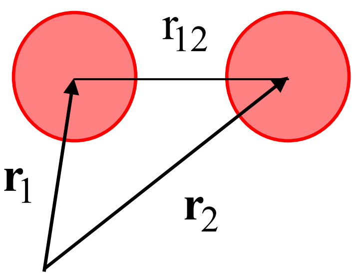
$$Z_N(V,T) = \int d\mathbf{r}_1\ldots d\mathbf{r}_N e^{-\beta U} = \int d\mathbf{r}^N e^{-\beta U}$$

$$\boxed{U(\mathbf{r}^N) = \sum_{i<j}^{N} u(|\mathbf{r}_i - \mathbf{r}_j|) = \sum_{i<j}^{N} u(r_{ij})}$$

assume pair-wise additivity

Define pair distribution function as: $g_N(\mathbf{r}_1,\mathbf{r}_2) = \dfrac{\rho_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)}{\rho_N^{(1)}(\mathbf{r}_1)\rho_N^{(1)}(\mathbf{r}_2)} \rightarrow 1$ for $r = r_{12} \rightarrow$ "$\infty$"

Isotropic fluid state (no crystal or external field) :



$\rho_N^{(1)}(r) = \dfrac{N}{V} = \rho$ : average number density

$\boxed{g_N(\mathbf{r}_1,\mathbf{r}_2) = g_N(|\mathbf{r}_1 - \mathbf{r}_2|) = g_N(r)}$ : NVT radial distribution function

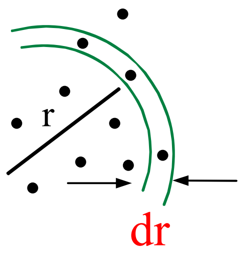
$$g_N(r) = \frac{\rho_N^{(2)}(r)}{\rho^2} = \frac{N(N-1)}{\rho^2}\int d\mathbf{r}_3 \dots d\mathbf{r}_N \, \frac{e^{-\beta U(\mathbf{r}^N)}}{Z_N}$$

$$g_N^{id}(r) = 1 - \frac{1}{N}$$

ideal gas :
U = 0 and $Z_N = V^N$

- $g_N$ measures pair correlations relative to ideal gas

$$\rho\int d\mathbf{r}\, g_N(r) = \frac{N(N-1)}{\rho}\underbrace{\int d\mathbf{r}_{12}}_{\frac{1}{V}\int d\mathbf{r}_1\, d\mathbf{r}_2}\int d\mathbf{r}_3 \dots d\mathbf{r}_N e^{-\beta U(\mathbf{r}^N)} / Z_N = N - 1$$



- $4\pi r^2 \rho\, g_N$ is average particle number in shell [r,r+dr] ( i.e. g(r) is conditional pdf )

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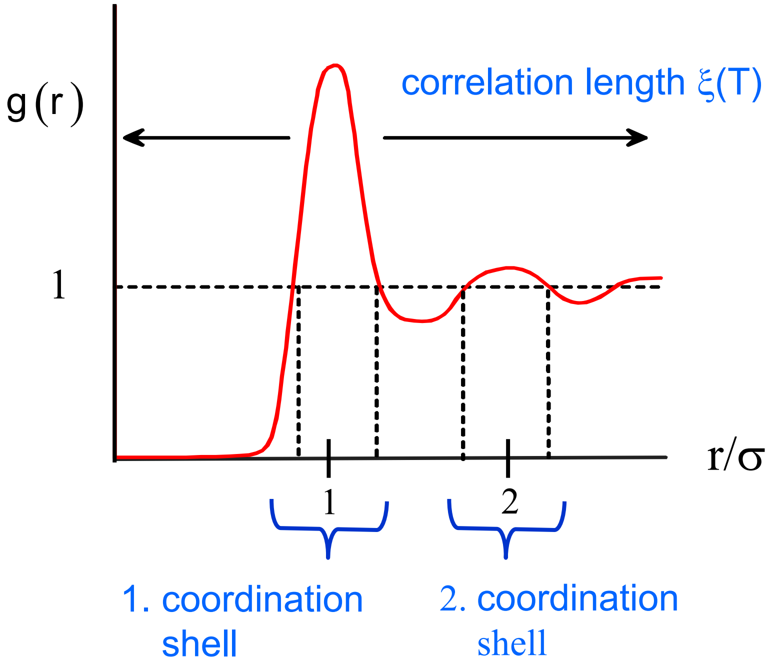
Thermodynamic limit for macroscopic system : $\boxed{g(r) = \lim_{N,V\to\infty} g_N(r)}$ $\rho$ = N/V fixed

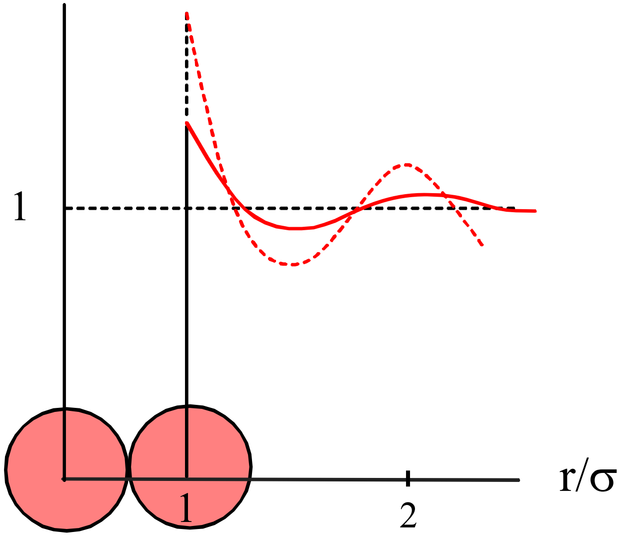
General behavior of g(r) :

- $g(r) \geq 0, \quad g(r \to \infty) = 1$
- $g(r) \cong 0, \quad$ when $\beta u(r) >> 1$
- $g(r) = \exp[-\beta u(r)]$ for $\rho \to 0$
- g(r) continuous where u(r) continuous

- Sketch of g(r) for soft pair potential



- Sketch of g(r) for hard-sphere dispersion

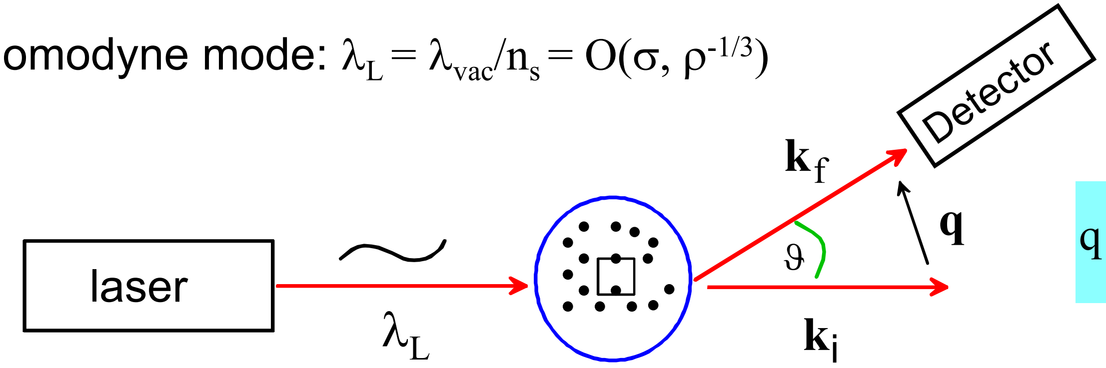


- jump at $r = \sigma$
- $g(r < \sigma) = 0$ since $u(r < \sigma) = \infty$
- $g(r) = \exp[-\beta u(r)] = \theta(r - \sigma)$ for $\rho = 0$

- Undulations in g(r) more pronounced for higher density and lower temperature

# Static light scattering and structure factor

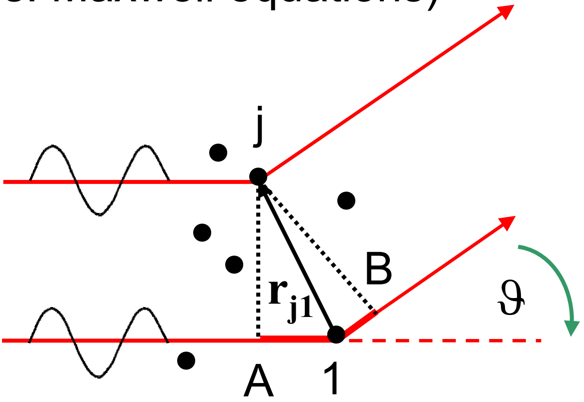
- Scattering in homodyne mode: $\lambda_L = \lambda_{vac}/n_s = O(\sigma, \rho^{-1/3})$



$$q = \frac{4\pi}{\lambda_L}\sin\frac{\vartheta}{2}$$

- Assumptions in basic scattering theory (more rigorous: Maxwell equations)

→ point scatterers (Rayleigh) : $\sigma << \lambda_L$
→ single scattering (1. Born approximation)
→ no absorption



Quasi-elastic : $k_f \approx k_i = 2\pi/\lambda_L \quad (\frac{h\nu}{c^2} = m_{ph} << M)$

Phase difference between j and 1 : $\overline{B}1 + \overline{A}1 = \mathbf{k}_f \cdot \mathbf{r}_{j1} - \mathbf{k}_i \cdot \mathbf{r}_{j1} = \mathbf{q} \cdot \mathbf{r}_{j1}$

Scattered el. field amplitude at detector :

$$E_s(\mathbf{q}) \propto \frac{1}{\lambda_L^2 R}\sum_{j=1}^{N}\exp\left\{i\,\mathbf{q}\cdot\left(\mathbf{r}_j-\mathbf{r}_1\right)\right\}$$

blue sky

R >> scatt. volume size

Time-averaged measured intensity : $I(q) = \left\langle E_s E_s^* \right\rangle_T \propto \left\langle \sum_{l,j=1}^{N} \exp\left\{ i\mathbf{q}\cdot\left(\mathbf{r}_l - \mathbf{r}_j\right)\right\} \right\rangle_T$

Ergodic system (fluid state) : $\lim_{T\to"\infty"} \langle \ldots \rangle_T = \langle \ldots \rangle_{N>>1}$

$$I(q) \propto N + \left\langle \sum_{l\neq j}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_{lj}} \right\rangle = N + N(N-1)\left\langle e^{i\mathbf{q}\cdot\mathbf{r}_{12}} \right\rangle = N + N(N-1)V\int d\mathbf{r}_{12}\, e^{i\mathbf{q}\cdot\mathbf{r}_{12}} \underbrace{\int d\mathbf{r}^{(N-2)} e^{-\beta U(\mathbf{r}^N)} / Z_N}_{\frac{1}{V^2} g_N(r_{12})}$$

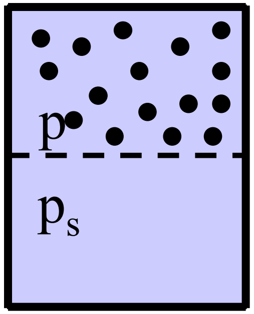
$$= N\left\{1 + \rho\int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} \left[g_N(r) - 1\right]\right\} + \underbrace{N\rho(2\pi)^3\delta(\mathbf{q})}$$

forward contribution
(no correlation information)

Static structure factor in T-limit :
(N → ∞, V → ∞ , ρ = N/V fixed)

$$S(q) = 1 + \rho\int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} \left[g(r) - 1\right] = \lim_{\infty} \left\langle \frac{1}{N} \delta\rho(\mathbf{q})\delta\rho(-\mathbf{q}) \right\rangle \geq 0$$

$$\delta\rho(\mathbf{q}) = \int d\mathbf{r}\; e^{i\mathbf{q}\cdot\mathbf{r}} \left\{ \sum_{l=1}^{N} \delta(\mathbf{r} - \mathbf{r}_l) - \rho \right\} = \sum_{l=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_l} - (2\pi)^3 \rho\, \delta(\mathbf{q})$$



Compressibility equation : $\lim_{q\to 0} S(q) = \frac{\chi_T}{\chi_T^{id}} = k_B T \left(\frac{\partial\rho}{\partial p}\right)_T$

# Remarks about ordering of T - limit and q → 0 limit

Periodic replication of system (scattering) volume V = $L^3$ :

$$V\delta_{\mathbf{q},0} = \int_V d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} \to (2\pi)^3\,\delta(\mathbf{q})$$

$$\frac{1}{V}\sum_{\mathbf{q}} F(\mathbf{q}) \to \frac{1}{(2\pi)^3}\int_{\mathbb{R}^3} d\mathbf{q}\, F(\mathbf{q})$$

regular at q = 0

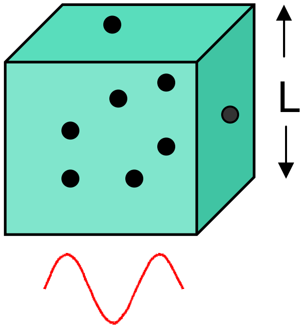
Applications :

$$\frac{(2\pi)^6}{V^2}\delta(\mathbf{q})^2 \to \delta^2_{\mathbf{q},0} = \delta_{\mathbf{q},0} \to \frac{(2\pi)^3}{V}\delta(\mathbf{q})$$

$$S_N(q) = \frac{1}{N}\left\langle \left|\delta\rho(\mathbf{q})\right|^2 \right\rangle_N \qquad \delta\rho(\mathbf{q}) = \sum_{l=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_l} - N\delta_{\mathbf{q},0}$$

$$\lim_{q\to0} S(q) = \lim_{q\to0}\lim_{\infty} S_N(q) = \frac{\chi_T}{\chi_T^{id}} \neq \lim_{\infty}\left\{S_N(q=0)=0\right\} = 0$$

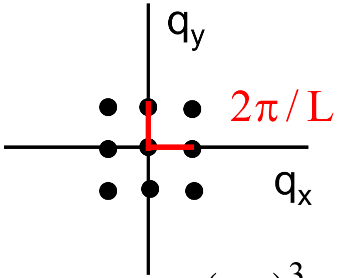
- First T-limit in NVT ensemble then q → 0
- Several wavelengths λ=2π/q should fit into V



$$f(\mathbf{r}+\mathbf{n}\,L) = f(\mathbf{r})$$

vector with components 0, ±1, ± 2, ...

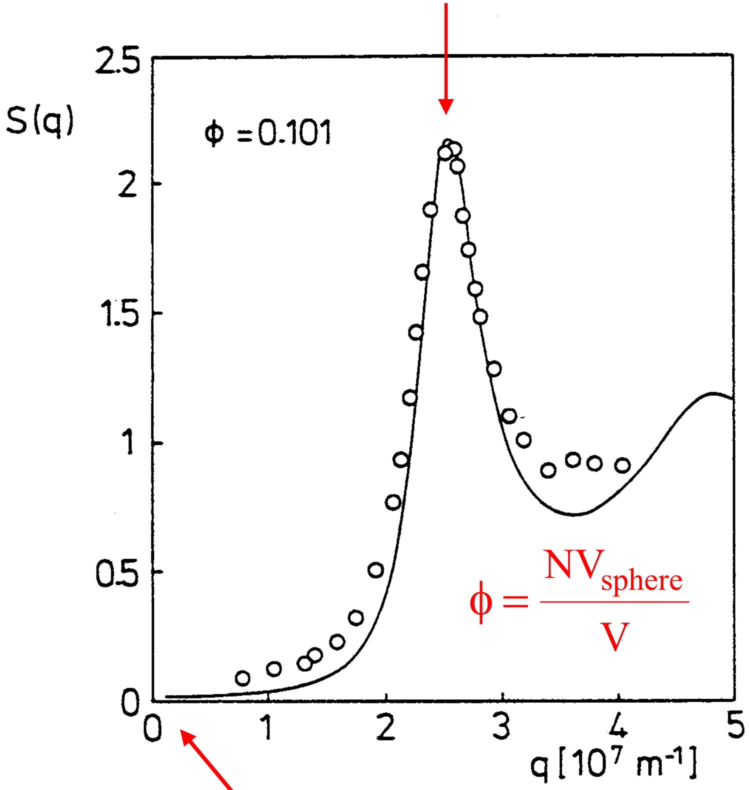
$$f(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{r}} \Rightarrow \mathbf{q} = \frac{2\pi}{L}\mathbf{n}$$



density of **q** points $= \frac{(2\pi)^3}{V}$

# S(q) and g(r) for a charge-stabilized dispersion

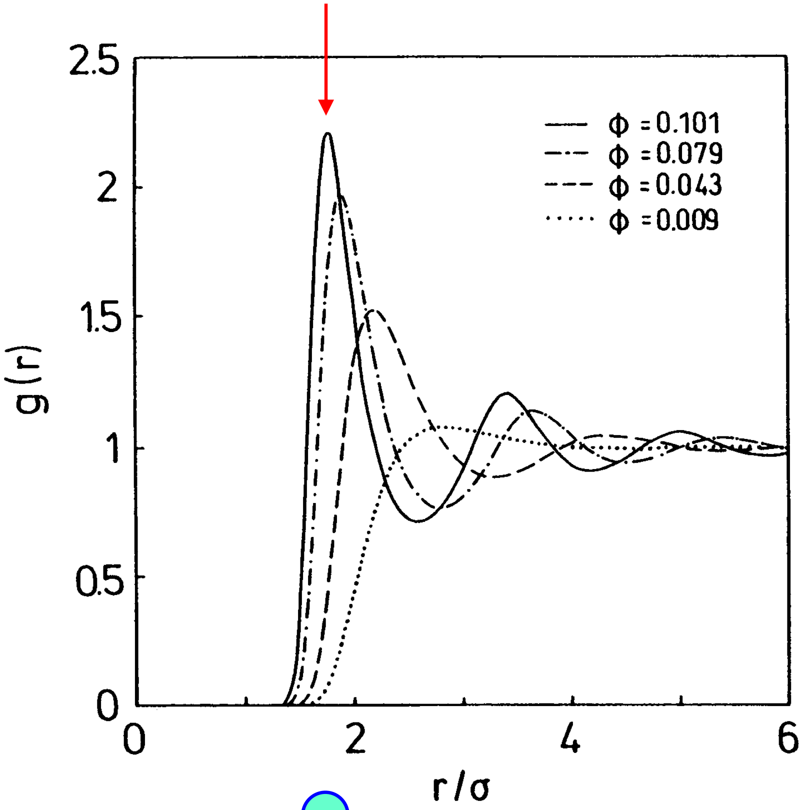
$q_m \approx 2\pi / r_m$

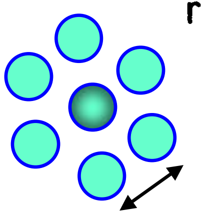


$$\phi = \frac{NV_{sphere}}{V}$$

low compressibility

$r_m$

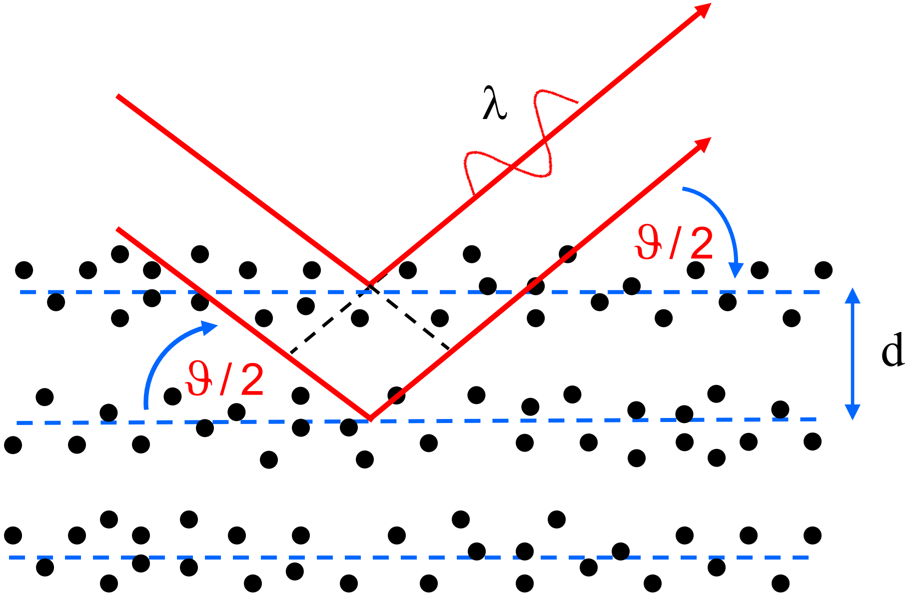




particle cage

(G. Nägele, Phys. Reports 272 (1996))

# Interpretation: diffusive Bragg scattering from particle density waves



1. order constructive interference

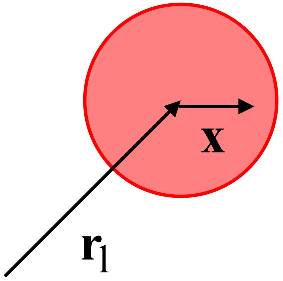
$$\frac{\lambda}{n_s} = 2d \sin\frac{\vartheta}{2}$$

$$q = \frac{4\pi n_s}{\lambda} \sin\frac{\vartheta}{2}$$

$$d \approx \frac{2\pi}{q}$$

typical spatial resolution for selected q

# Point scatterers → weakly scattering colloidal spheres with a = O(λ)



$$E_s(\mathbf{q}) \propto \sum_{l=1}^{N} \int_{x<a} d\mathbf{x}\, e^{i\mathbf{q}\cdot[\mathbf{r}_l+\mathbf{x}]}\psi(\mathbf{x})$$

$$\propto \left( \int_{x<a} d\mathbf{x}\, e^{i\mathbf{q}\cdot\mathbf{x}}\psi(\mathbf{x}) \right) \sum_{l=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_l}$$

$$\psi(\mathbf{x}) = \varepsilon_p(\mathbf{x}) - \varepsilon_s$$

local
scattering strength

$$\boxed{I(q) \propto \langle N \rangle P(q) S(q)}$$

Single-particle form factor

$$\boxed{P(q) = \left| \frac{\int_0^a d\mathbf{x}\, e^{i\mathbf{q}\cdot\mathbf{x}}\psi(\mathbf{x})}{\int_0^a d\mathbf{x}\, \psi(\mathbf{x})} \right|^2}$$

$$P(q=0)=1$$

$$P(q=\infty)=0$$

Inherent assumptions :

→ isotropic spheres

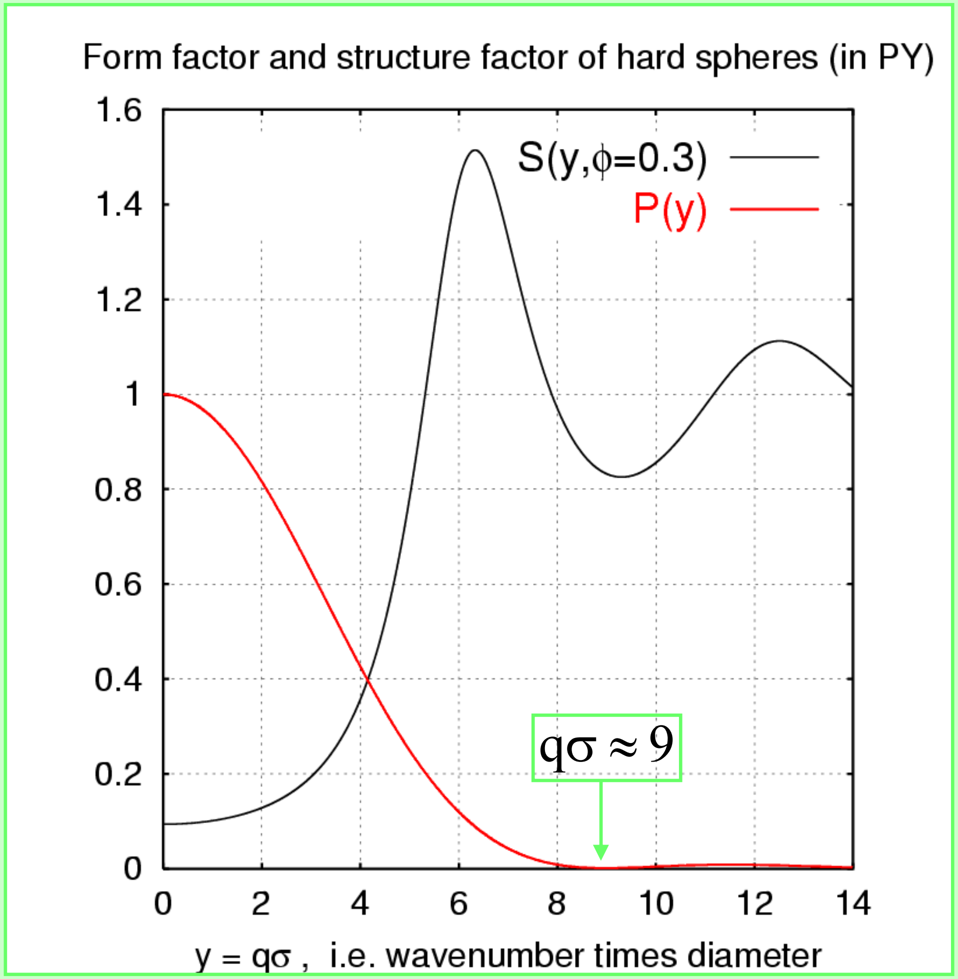
→ Rayleigh-Gans-Debye (RGD) regime :
no phase difference of light through particle and solvent, respectively, i.e

$$2\pi|n_p - n_s| a/\lambda < 0.1$$

# Example: optically uniform colloidal spheres with $\Psi$ = const

$$P(q) = \left( \frac{3 j_1(qa)}{qa} \right)^2 = \left( b(q) \right)^2$$

Formamplitude



- Large particles scatter more strongly in forward direction
- q > 4.5/a not accessible by light scattering

# Methods of calculation

- Computer simulations (Monte-Carlo, MD and BD)
- → Ornstein-Zernike-type integral equation schemes

Introduce total correlation function : $h(r_{12}) := g(r_{12}) - 1$ $h(r_{12}) \to 0$ , for $r_{12} \to \infty$

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

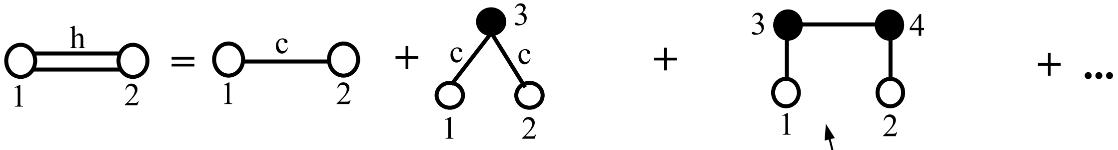
$$\boxed{h(r_{12}) = c(r_{12}) + \rho \int d\mathbf{r}_3\, c(r_{13}) h(r_{23})}$$

total correlations of 1 and 2

direct correlations

indirect correlations of 1 and 2 through particles 3,4,…

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



$$\overset{i}{\bullet} = \rho \int d\mathbf{r}_i$$

indirect correlations of 1 and 2 through two intermediate particles 3 and 4

General properties of c(r) : $c(r) = h(r) = e^{-\beta u(r)} - 1 + O(\rho)$

$$\boxed{c(r) = -\beta u(r), \quad r \to \infty}$$

valid for all densities

- c(r) is more amenable to approximations than g(r)

- Fourier-transformed OZ equation from convolution theorem :

$$S(q) = 1 + \rho \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} h(r) = 1 + \rho\, h(q) \qquad h(q) = \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} h(r) = \frac{4\pi}{q} \int_0^\infty dr\, r \sin(qr)\, h(r)$$

$$h(q) = c(q) + \rho\, c(q)\, h(q)$$

- Solving for Fourier-transformed c(r) gives S(q) in terms of c(q) :

$$S(q) = \frac{1}{1 - \rho\, c(q)} \geq 0$$

---

Ornstein-Zernike equation

\+ approximate closure relation : c(r) = Functional of h(r’) & u(r’)

\+ zero overlap condition (HC) : g(r < σ) = 0

⇨

Closed integral equation for g(r) = h(r) –1

# Examples of important closure relations

- Rescaled mean spherical approximation (RMSA) :

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

- Hypernetted chain approximation (HNC)

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

- Percus-Yevick approximation (PY)

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

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

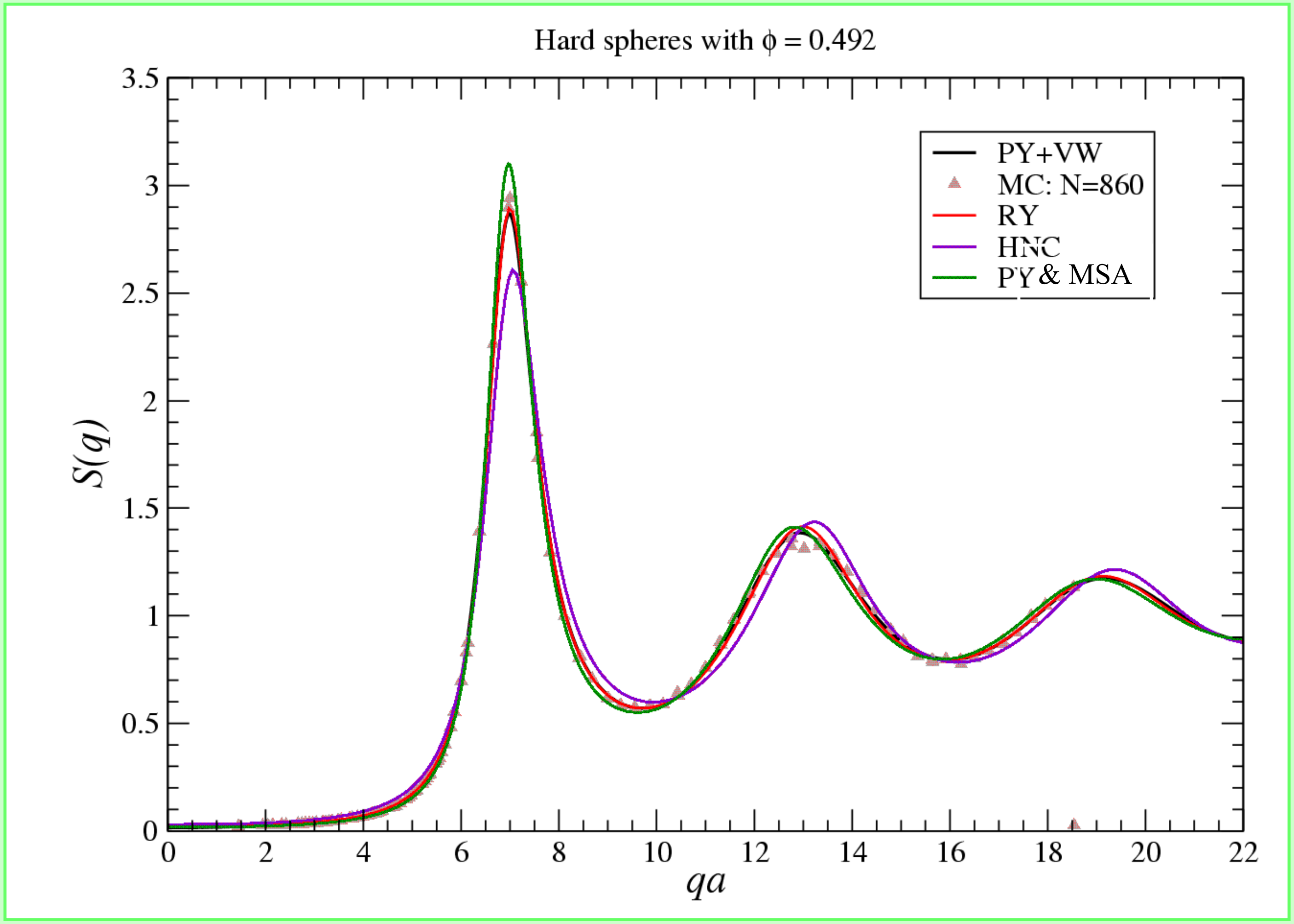
$$c(r) = e^{-\beta u(r)} \cdot \left[ 1 + \frac{\exp\{\gamma(r)\, f(r)\} - 1}{f(r)} \right] - \gamma(r) - 1 \qquad\qquad f(r) = 1 - e^{-\alpha r}$$

$\alpha \to \infty$ : HNC

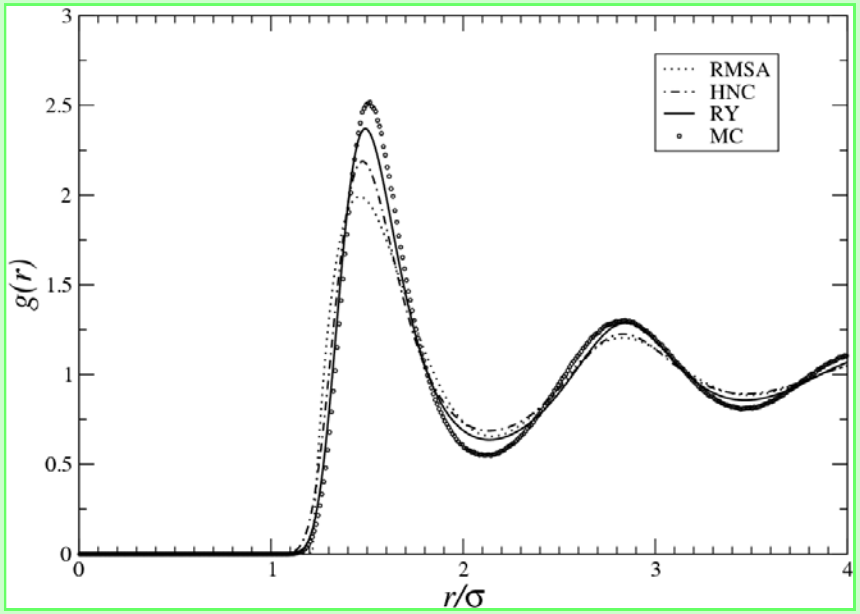
$\alpha \to 0$ : PY

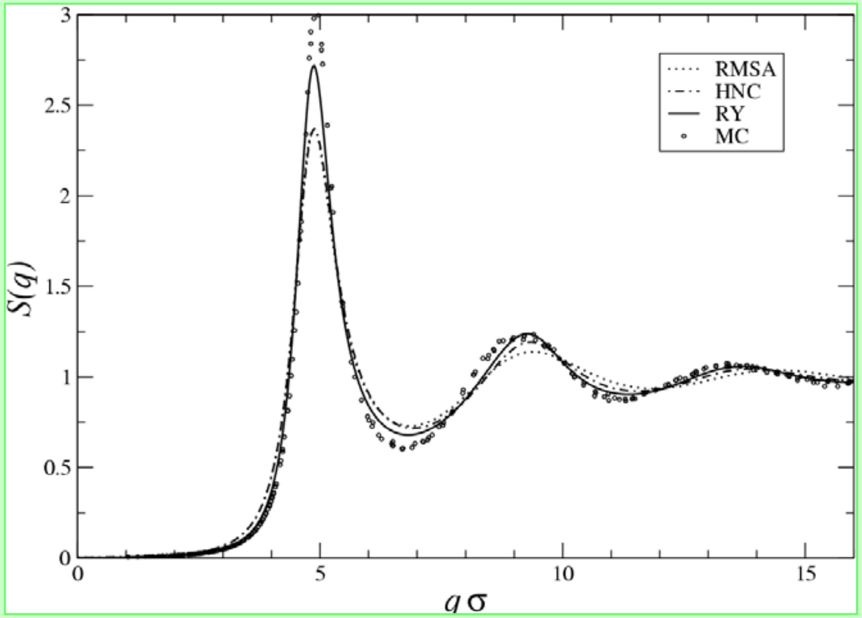
$$\chi_T^{\mathrm{Virial}} \underset{\uparrow}{=} \chi_T^{\mathrm{Compr}}$$

determines $\alpha$


Hard spheres with ϕ = 0.492
S(q)
qa
3.5
3
2.5
2
1.5
1
0.5
0
0
2
4
6
8
10
12
14
16
18
20
22
PY+VW
MC: N=860
RY
HNC
PY & MSA

# Example: strongly coupled charge-stabilized colloidal spheres ($\phi$ = 0.185)





Results by Banchio & Nägele :
see in Lecture Notes 14, Polish Academy of Science Publishing, Warsaw (2004)

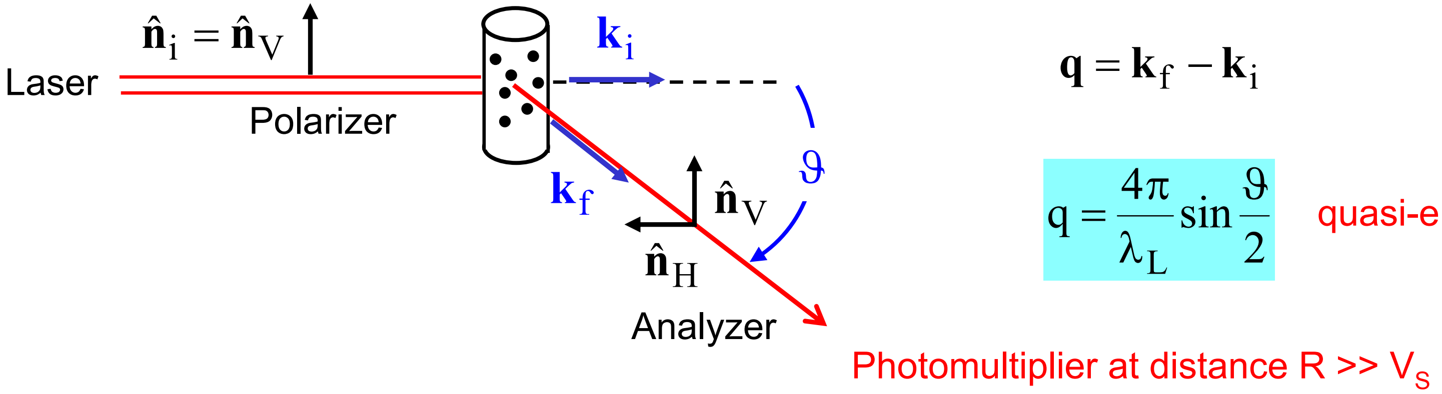
- For each u(r), closures should be tested first against simulations

# 3. Dynamic light scattering

- **Basic scattering theory**
- **Dynamic correlation functions**

# Basic scattering theory

- Homodyne scattering set-up :



$$\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$$

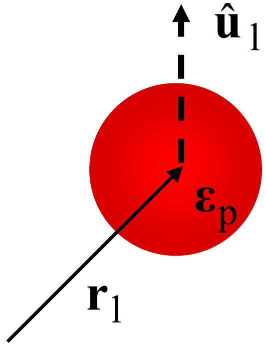
$$\boxed{q = \frac{4\pi}{\lambda_L}\sin\frac{\vartheta}{2}}$$ quasi-elastic

→ Maxwell equations for non-magnetic and linear dielectric media

→ Single scattering (1. Born approximation)

→ RGD regime (superposition + s-waves)

- Scattered electric field strength at detector place :



$$\mathbf{E}_S(\mathbf{q}) \propto \frac{e^{ik_i\cdot R}}{\lambda^2 R}\mathbf{E}_0\sum_{l=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_l}\,\hat{\mathbf{n}}_f\cdot(\mathbf{1}-\hat{\mathbf{k}}_f\hat{\mathbf{k}}_f)\cdot\mathbf{B}_l(\mathbf{q})\cdot\hat{\mathbf{n}}_i$$

far-field electric field ⊥ propagation direction

---

$$\mathbf{B}_l(\mathbf{q}) = \frac{1}{\varepsilon_s}\int_{x\le a} d\mathbf{x}\; e^{i\mathbf{q}\cdot\mathbf{x}}\left[\boldsymbol{\varepsilon}_p(\mathbf{x})-\varepsilon_s\mathbf{1}\right]$$

form amplitude tensor of sphere l

$$\mathbf{B}_l(\mathbf{q}) = \frac{V_a}{\varepsilon_s}b(q)\left\{\left(\varepsilon_p^{\|}-\varepsilon_s\right)\hat{\mathbf{u}}_l\hat{\mathbf{u}}_l+\left(\varepsilon_p^{\perp}-\varepsilon_s\right)\left(\mathbf{1}-\hat{\mathbf{u}}_l\hat{\mathbf{u}}_l\right)\right\}$$

homog. sphere with single optical axis pointing along unit vector $\hat{\mathbf{u}}_l$

form amplitude of isotrop & uniform sphere

- VV – geometry : measuring non-depolarized el. field comp.
- VH – geometry : measuring depolarized el. field comp → rotational diffusion
- Optically isotropic sphere : $\boldsymbol{\varepsilon}_p = \varepsilon_p\mathbf{1}$ → zero VH – singe scattering

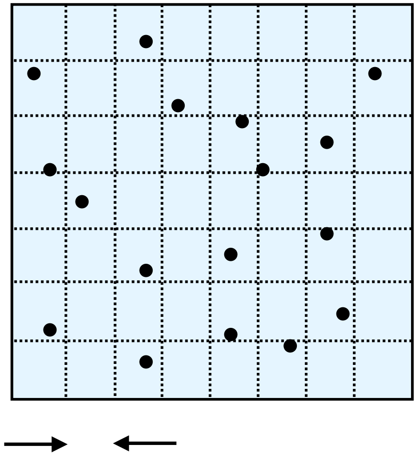
# Siegert relation: polarized scattering from isotropic & monodisperse colloidal spheres

Homodyne DLS: determines intensity autocorrelation function (IACF)

$$g_I(q,t) = \langle I_s(\mathbf{q},0) I_s(\mathbf{q},t)\rangle = \langle E_s(\mathbf{q},0)\, E_s^*(\mathbf{q},0) \cdot E_s(\mathbf{q},t)\, E_s^*(\mathbf{q},t)\rangle$$

time average

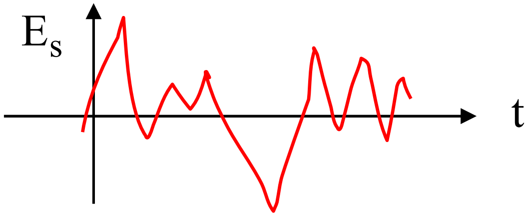
$$\begin{aligned} g_I(q,t) = & \langle E_s(\mathbf{q},0)\, E_s^*(\mathbf{q},0)\rangle \langle E_s(\mathbf{q},t)\, E_s^*(\mathbf{q},t)\rangle \\ & + \langle E_s(\mathbf{q},0)\, E_s(\mathbf{q},t)\rangle \langle E_s^*(\mathbf{q},0)\, E_s^*(\mathbf{q},t)\rangle \\ & + \langle E_s(\mathbf{q},0)\, E_s^*(\mathbf{q},t)\rangle \langle E_s^*(\mathbf{q},0)\, E_s(\mathbf{q},t)\rangle \end{aligned}$$



> Correlation length

Central limit theorem:
- each cell includes many scatterers
- $E_s$ is complex central Gaussian random variable

$$g_I(q,t) = \langle I_s(\mathbf{q})\rangle^2 + 0 + \langle E_s(-\mathbf{q},0)\, E_s(\mathbf{q},t)\rangle^2$$



isotropic fluid phase

time-indep. mean in equilibrium

translational invariance of homog. system

$$\left\langle e^{i\mathbf{q}\cdot\left[\mathbf{r}_j+\mathbf{r}_l\right]}\right\rangle = \left\langle e^{i\mathbf{q}\cdot\left[\mathbf{r}_j+\mathbf{a}+\mathbf{r}_l+a\right]}\right\rangle = \underbrace{\left\langle e^{i\mathbf{q}\cdot\left[\mathbf{r}_j+\mathbf{r}_l\right]}\right\rangle}_{=\,0} e^{2i\mathbf{q}\cdot\mathbf{a}}$$

spatial homogeneity

$$\left\langle e^{i\mathbf{k}_1\cdot\mathbf{r}_1}\, e^{i\mathbf{k}_2\cdot\mathbf{r}_2}\, \ldots\, e^{i\mathbf{k}_n\cdot\mathbf{r}_n}\right\rangle = \delta_{\mathbf{k}_1+\mathbf{k}_2+\ldots+\mathbf{k}_n,0}\left\langle e^{i\mathbf{k}_1\cdot\mathbf{r}_1}\, e^{i\mathbf{k}_2\cdot\mathbf{r}_2}\, \ldots\, e^{i\mathbf{k}_n\cdot\mathbf{r}_n}\right\rangle$$

---

$$\boxed{g_E(q,t) = \left\langle E_s^*(\mathbf{q},0)\; E_s(\mathbf{q},t)\right\rangle}$$

el. field autocorrelation function (EFAC)

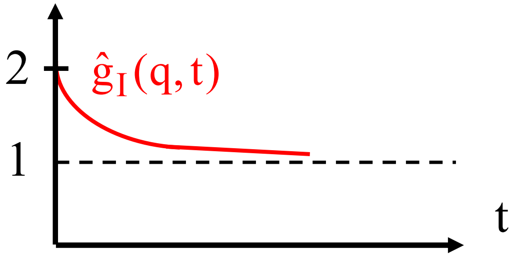
$$\boxed{g_E(q,t) = \left[g_I(q,t) - \left\langle I_s(\mathbf{q})\right\rangle^2\right]^{1/2}}$$

Siegert relation for stationary, ergodic system

( time average → ensemble average )

$$\hat{g}_E(q,t) = g_E(q,t)/\left\langle I_s(\mathbf{q})\right\rangle \quad \rightarrow \quad \hat{g}_E(q,0) = 1$$

$$\hat{g}_I(q,t) = g_I(q,t)/\left\langle I_s(\mathbf{q})\right\rangle^2 \quad \rightarrow \quad \hat{g}_I(q,0) = \left\langle I_s(\mathbf{q})^2\right\rangle/\left\langle I_s(\mathbf{q})\right\rangle^2$$



$$\boxed{\hat{g}_I(q,t) = 1 + \left[\hat{g}_E(q,t)\right]^2}$$

$$0 \le \left\langle\left[I_s(\mathbf{q}) - \left\langle I_s(\mathbf{q})\right\rangle^2\right]\right\rangle = \left\langle I_s(\mathbf{q})^2\right\rangle - \left\langle I_s(\mathbf{q})\right\rangle^2 \;\rightarrow$$

in general, only valid that : $\hat{g}_I(q,0) \ge 1$

# Dynamic correlation functions

- Homodyne DLS experiment + Siegert relation :

$$\boxed{g_E(q,t) \propto \langle N \rangle P(q)\, S(q,t)}$$

← dynamic structure factor

(t > $\tau_{DLS} \approx 1\ \mu$sec)

$$S(q,t) = \lim_{\infty} \left\langle \frac{1}{N} \delta\rho(-\mathbf{q},0)\, \delta\rho(\mathbf{q},t) \right\rangle = \lim_{\infty} \left\{ \frac{1}{N} \sum_{j,l=1}^{N} \left\langle e^{i\mathbf{q}\cdot\left[\mathbf{r}_j(t)-\mathbf{r}_l(0)\right]} \right\rangle - N\,\delta_{\mathbf{q},0} \right\}$$

$$S(q) = S(q,0) = 1 + \rho \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} \left[g(r) - 1\right]$$

$$\delta\rho(\mathbf{q}) = \sum_{l=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_l} - N\delta_{\mathbf{q},0}$$

$$\boxed{S(q,t) = G(q,t) + S_d(q,t)}$$

← split in self- and distinct parts

$$S_d(q,t) = \lim_{\infty} \left\langle (N-1) e^{i\mathbf{q}\cdot[\mathbf{r}_1(t)-\mathbf{r}_2(0)]} - N\delta_{\mathbf{q},0} \right\rangle = \rho \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} \left\{ \underbrace{\lim_{\infty} \left\langle V\delta\left(\mathbf{r} - \mathbf{r}_1(t) + \mathbf{r}_2(0)\right) \right\rangle} - 1 \right\}$$

$$S_d(q,t) = \rho \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} \left\{ g_d(r,t) - 1 \right\}$$

$g_d(r,t)$: distinct van Hove real-space function (2d – experiments)

$$g_d(r,0) = g(r)$$

- Self-dynamic scattering function G(q,t) :

$$G(q,t) = \lim_{\infty} \left\langle e^{i\mathbf{q}\cdot[\mathbf{r}_1(t)-\mathbf{r}_1(0)]} \right\rangle = \rho \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} g_s(r,t)$$

$$g_s(r,t) = \lim_{\infty} \left\langle \delta\left(\mathbf{r} - \mathbf{r}_1(t) + \mathbf{r}_1(0)\right) \right\rangle$$

self van Hove function
(single-particle conditional pdf)

---

- Small-q expansion for isotropic system :

$$G(q,t) = 1 - \frac{1}{2} \sum_{\alpha=1}^{d} q_\alpha{}^2 \underbrace{\left\langle [x_{\alpha 1}(t) - x_{\alpha 1}(0)]^2 \right\rangle}_{\left\langle [\mathbf{r}_1(t) - \mathbf{r}_1(0)]^2 \right\rangle / d} + O(q^4)$$

Mean squared displacement

$$\boxed{W(t) = \frac{1}{2d} \left\langle [\mathbf{r}_1(t) - \mathbf{r}_1(0)]^2 \right\rangle}$$

d = 1, 2 and 3 (dimensionallity)

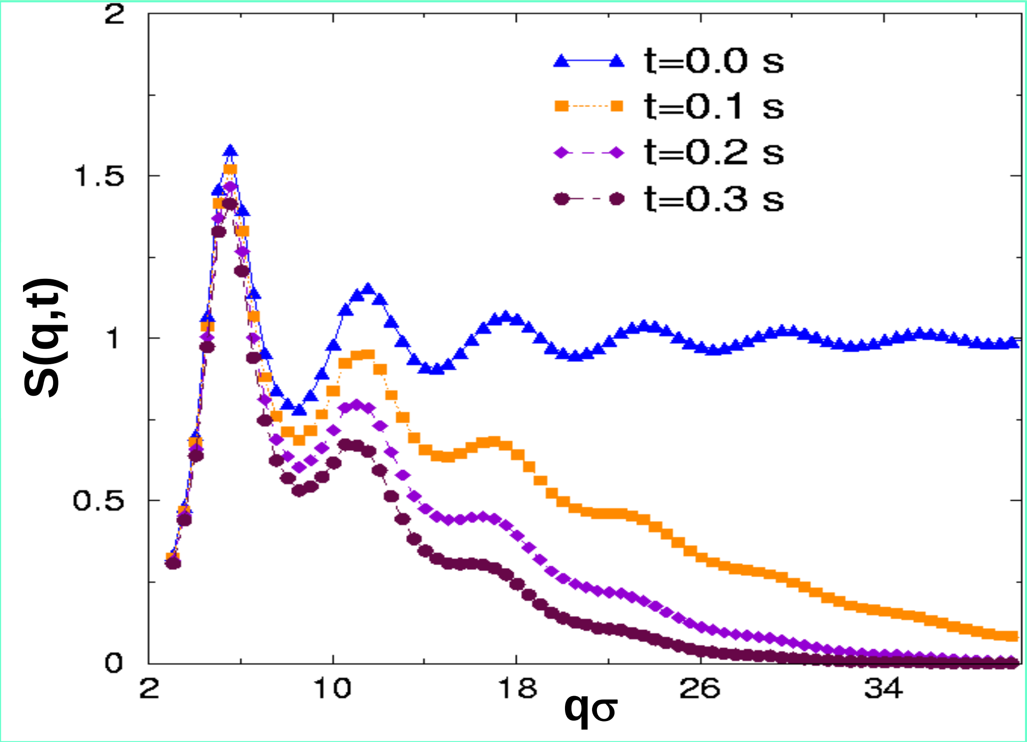
- Expansion in cumulant form :

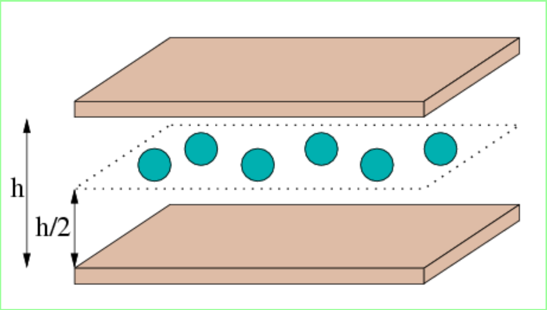
$$G(q,t) = \exp\left\{-q^2 W(t)\right\} \cdot \left[1 \;+\; \text{non-Gaussian terms of } O(q^4)\right]$$

$$g_s(r,t) = \left(4\pi W(t)\right)^{-d/2} \exp\left\{-\frac{r^2}{4W(t)}\right\} \;+\; \text{non-Gaussian terms}$$

Small in fluid phase but:
dynamic heterogeneities
In colloidal glasses

# Example: Quasi-2D dynamic structure factor of charged colloidal spheres



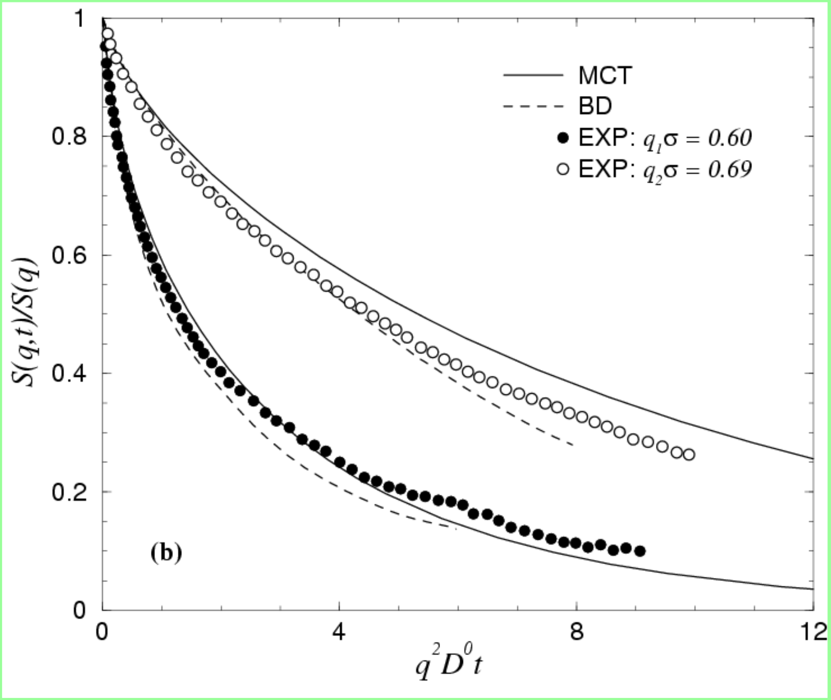


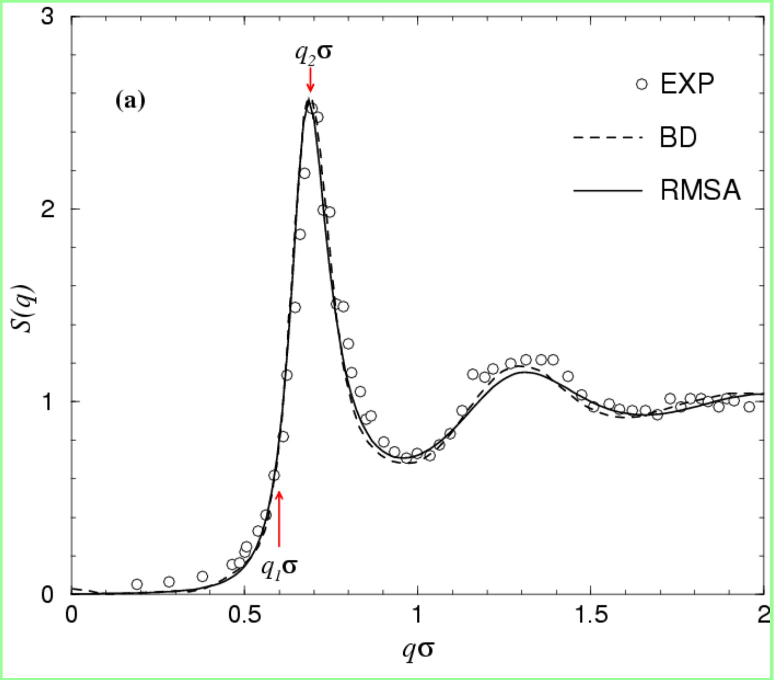
( Courtesy: J.L. Arauz-Lara, Univ. of San Luis Potosi )

$$S(q, t = 0) = S(q)$$

$$S(q, t \rightarrow \infty) = 0$$ (in fluid phase)

# Example: Dynamic structure factor of 3D charge-stabilized dispersion

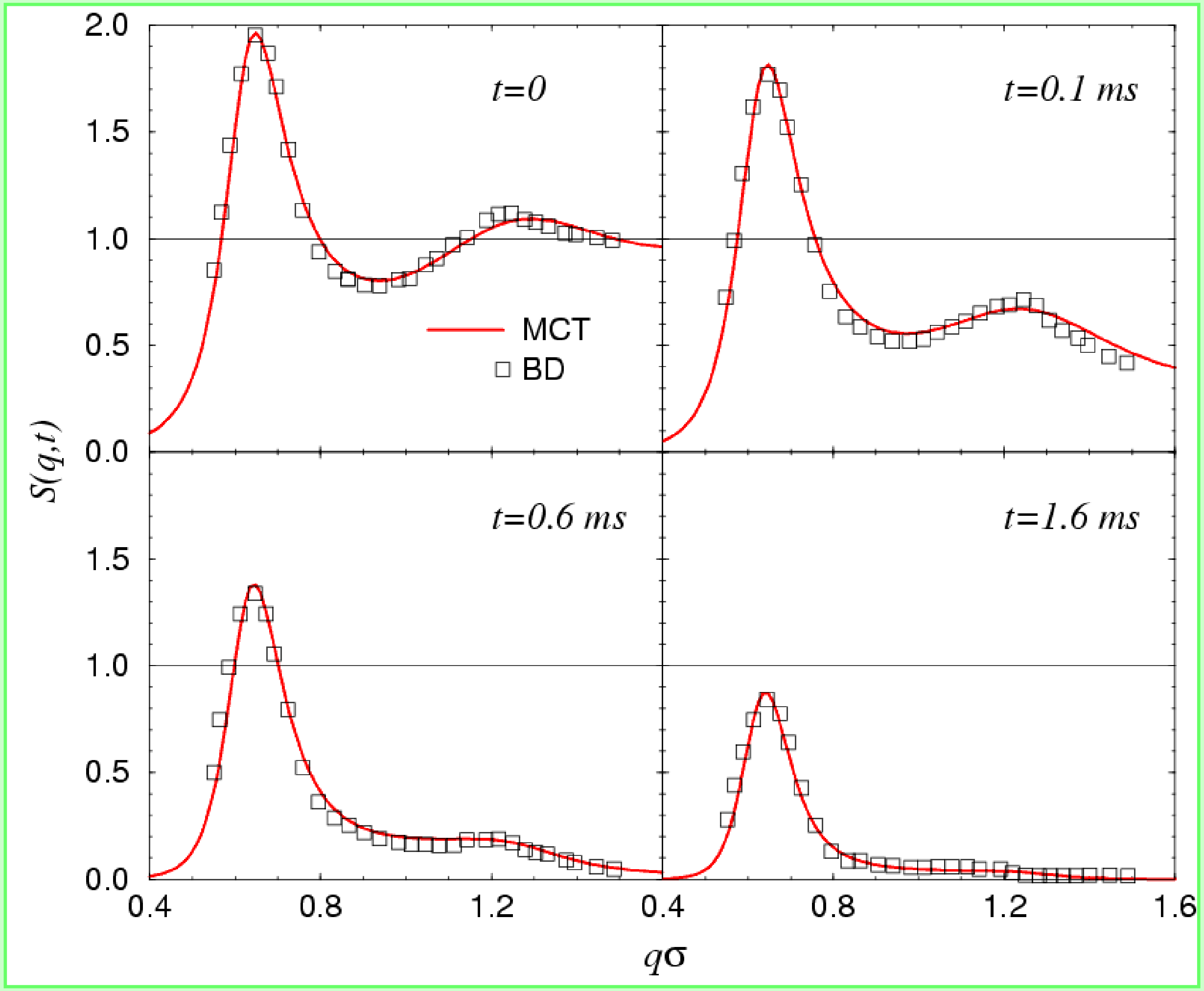




(Banchio, Nägele & Bergenholtz, J. Chem. Phys. 113 (2000))

- Density autocorrelation function S(q,t) decays monotonically in t
- Valid for any regular autocorrelation function at colloidal time scales

# Example: Dynamic structure factor of 3D charge-stabilized dispersion

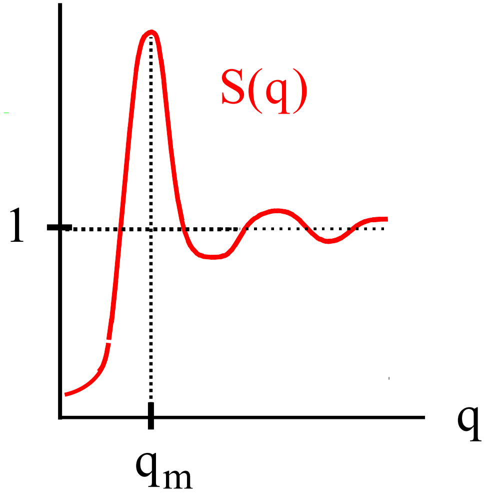


BD : Gaylor et al., J. Phys. A (1980)

Theory : Banchio, Nägele & Bergenholtz, J. Chem. Phys. (2000)

# How to measure G(q,t) and W(t) using DLS ?

- Large-q measurement :



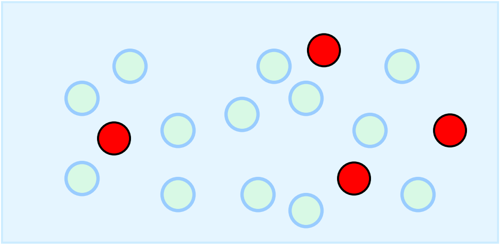
$$S(q,t) = G(q,t) + S_d(q,t) \approx G(q,t) \quad (q > q_m)$$

$$S_d(q,0) = S(q) - 1$$

$$G(q,0) = 1$$

- Binary mixture of, w/r to interactions, identical tracer and host spheres

$$g_E(q,t) \propto G(q,t)$$

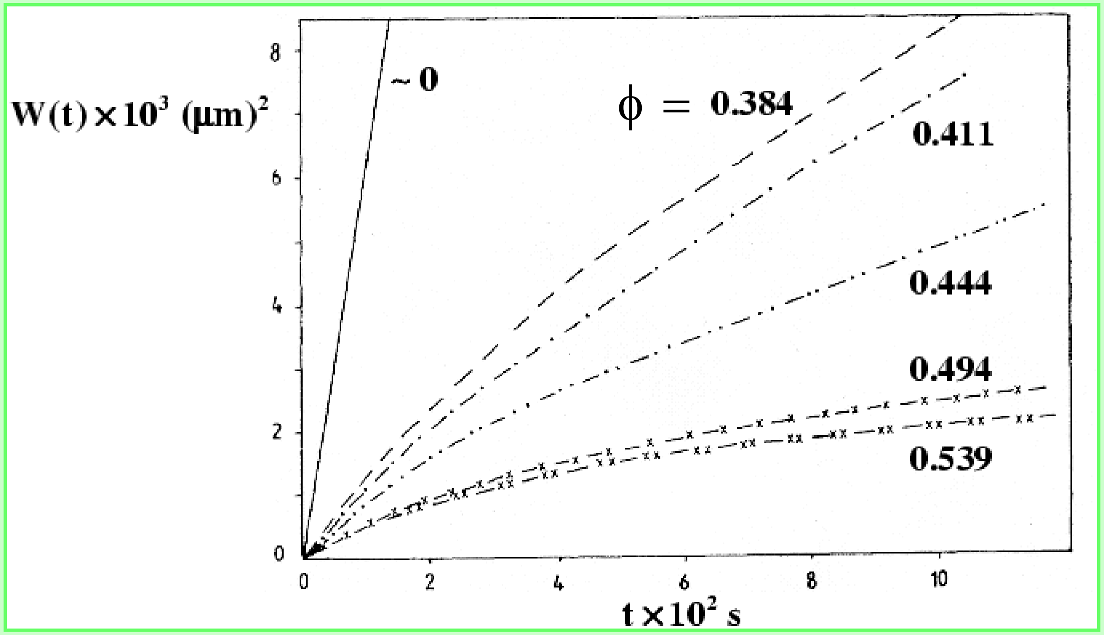


$$(\rho_T \ll \rho_H)$$

- DLS: typical resolution of correlation times

$1\ \mu$sec $<$ t $<$ sec. to days

# Example: Silica tracer spheres in index-matched PMMA sphere solution



(van Megen et al., J. Chem. Phys. 85 (1986))

- Plot - log $G(q,t)/q^2$ versus $q^2$ and extrapolate to $q \rightarrow 0$ (then zero non-Gaussian contr.)
- Strong many-body influence of HI for $\phi > 0.2$

# 4. Theoretical description of colloid dynamics

- **Single particle dynamics in very dilute dispersions**
- **Colloidal time and length scales**
- **Generalized Smoluchowski diffusion equation for dense systems**

# Single particle dynamics in very dilute dispersions

- Langevin equation for a single colloidal sphere :

$$\boxed{M\frac{d}{dt}\mathbf{v}(t) = -\zeta_0\,\mathbf{v}(t) + \mathbf{F}(t)} \qquad (t \gg \tau_s)$$

Gaussian & Markovian random solvent forces

$$\langle F_\alpha(t)\rangle_F = 0$$

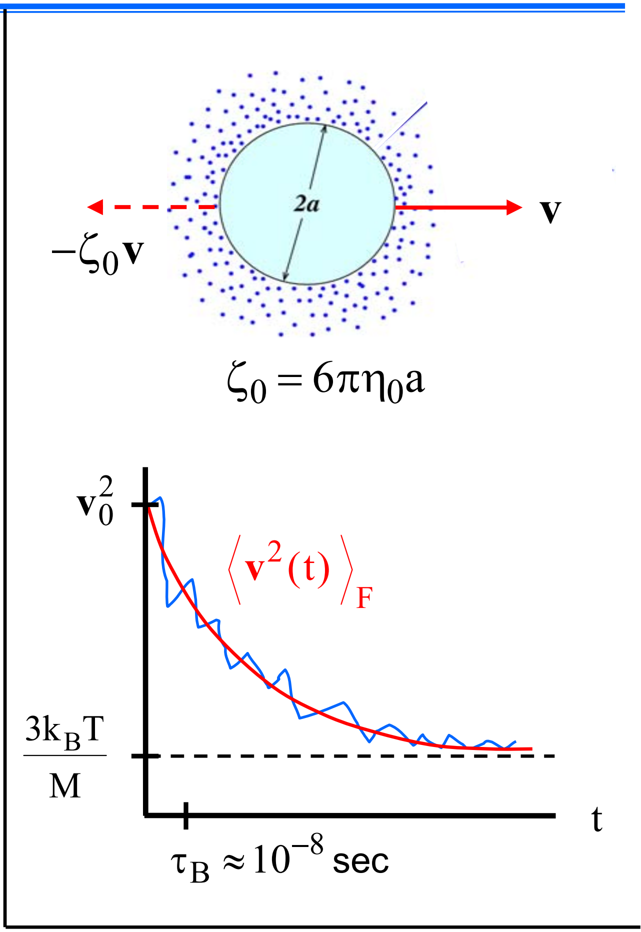
$$\langle F_\alpha(t)F_\beta(t')\rangle_F = 2\Gamma\,\delta_{\alpha\beta}\,\delta(t-t')$$ isotropic white noise

$$\langle \mathbf{v}(t)\rangle_F = \mathbf{v}_o e^{-t/\tau_B} \qquad \boxed{\tau_B = M/\zeta_0}$$ momentum relaxation time

$$\mathbf{v}(t) = \mathbf{v}_o e^{-t/\tau_B} + \int_0^t du\, e^{-(t-u)/\tau_B}\,\mathbf{F}(\mathbf{u})/M$$

$$\langle \mathbf{v}^2(t)\rangle_F = \mathbf{v}_0^2\, e^{-2t/\tau_B} + \frac{3\Gamma}{M\zeta_0}\left(1-e^{-2t/\tau_B}\right) \xrightarrow[(t\gg\tau_B)]{} \langle \mathbf{v}^2\rangle_{eq} = \frac{3k_BT}{M}$$ equipartition theorem

$$\boxed{\Gamma = k_BT\,\zeta_0}$$ Fluctuation-dissipation relation



- Ensemble of independent particles in equilibrium → stationarity in time

$$\langle\ldots\rangle = \int d\mathbf{r}_0 \int d\mathbf{v}_0\, P_{eq}(\mathbf{r}_0,\mathbf{v}_0)\langle\ldots\rangle_F \qquad P_{eq}(\mathbf{r}_0,\mathbf{v}_0) = \frac{1}{V}\left(\frac{M}{2\pi k_B T}\right)^{3/2} e^{-\frac{M}{2k_B T}\mathbf{v}_0^2}$$

$$\phi_v(|t'-t''|) = \frac{1}{d}\langle \mathbf{v}(t')\cdot\mathbf{v}(t'')\rangle$$

velocity autocorrelation function (VAF)

$$\phi_v(t) = \frac{1}{3}\langle \mathbf{v}(t)\cdot\mathbf{v}_0\rangle = \frac{k_B T}{M} e^{-t/\tau_B}$$

single-sphere VAF

$$\mathbf{r}(t)-\mathbf{r}_0 = \int_0^t dt'\,\mathbf{v}(t') \quad \longrightarrow \quad W(t) = \frac{1}{2d}\left\langle (\mathbf{r}(t)-\mathbf{r}_0)^2 \right\rangle = \frac{1}{2}\int_0^t dt' \int_0^t dt''\,\phi_v(|t'-t''|)$$

$$W(t) = \int_0^t du\,(t-u)\,\phi_v(u)$$

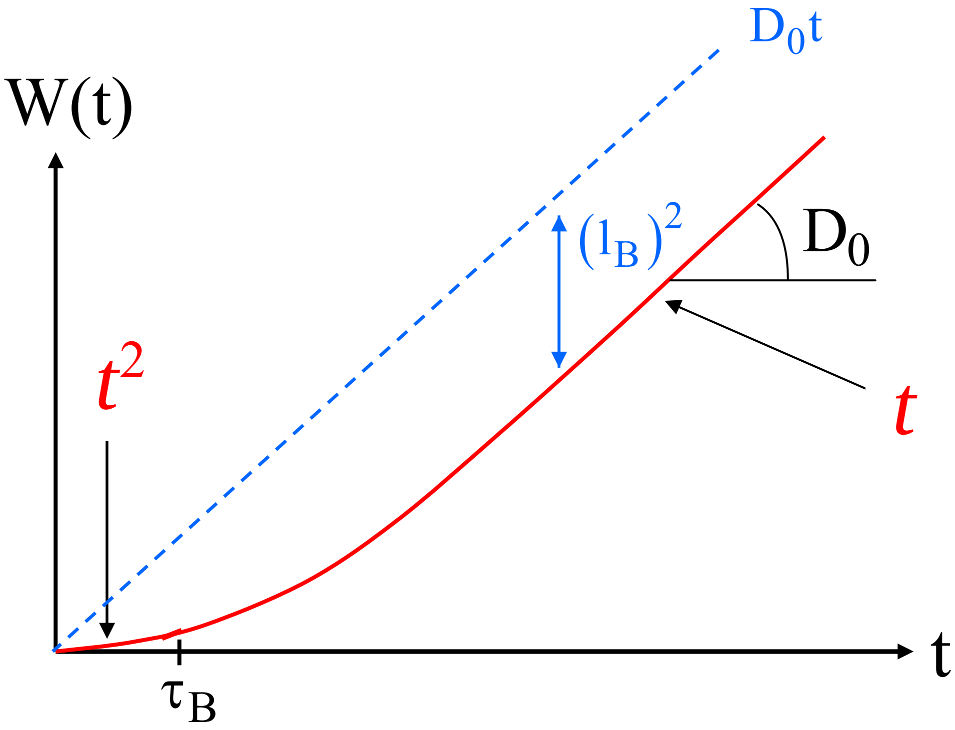
Ornstein-Fürth formula for stationary system

$$W(t) = D_0 t\left[1-\frac{\tau_B}{t}\left(1-e^{-t/\tau_B}\right)\right] \to \begin{cases} \dfrac{k_B T}{2M}t^2 & (\tau_s \ll t \ll \tau_B) \\ D_0(t-\tau_B) & (\tau_B \ll t) \end{cases}$$

$$D_0 = \frac{k_B T}{\zeta_0}$$

single-sphere translational Stokes-Einstein relation

Single-sphere mean squared displacement (MSD)



- Displacement $\Delta\mathbf{r} = \mathbf{r}(t) - \mathbf{r}_0$ is central Gaussian random variable w/r to <…>

$$P(\Delta\mathbf{r},t) = \prod_{\alpha=1}^{3}\left(2\pi\,\sigma_{\Delta x_\alpha}\right)^{-1/2} \exp\left\{-\frac{(\Delta x_\alpha)^2}{2\,\sigma^2_{\Delta x_\alpha}}\right\} \qquad \sigma^2_{\Delta x_\alpha} = \left\langle (\Delta x_\alpha)^2 \right\rangle = 2W(t)$$

$$P(\Delta\mathbf{r},t) = \left(4\pi W(t)\right)^{-3/2} \exp\left\{-\frac{(\Delta\mathbf{r})^2}{4\,W(t)}\right\} \qquad P(\Delta\mathbf{r},t=0) = \delta\left(\Delta\mathbf{r}\right)$$

- Pdf is fundamental solution of diffusion-like equation:
  (not a Fokker-Planck equation, since $\Delta\mathbf{r}$ Gaussian but non-Markovian)

$$\frac{\partial}{\partial t}P(\Delta\mathbf{r},t) = D^*(t)\,\nabla^2 P(\Delta\mathbf{r},t) \qquad D^*(t) = \frac{d}{dt}W(t) = D_0\left[1 - e^{-t/\tau_B}\right]$$

- Single-particle self-dynamic structure factor :

$$G(q,t) = \int d(\Delta\mathbf{r})e^{i\mathbf{q}\cdot\Delta\mathbf{r}}\,P(\Delta\mathbf{r},t) = e^{-q^2 W(t)} \rightarrow e^{-q^2 D_0 t}$$

$\Delta t \gg \tau_B$ & $\Delta x \gg \sqrt{D_0 \tau_B}$

# Overdamped (positional) Langevin equation for a single particle

- Time required to diffuse a distance comparable to a = 100 nm :

$$\tau_I = \frac{a^2}{D_0} \approx 10^{-3}\ \text{sec} \longrightarrow \boxed{\tau_I \gg \tau_B}$$

Momenta relaxed long before observable change in particle configuration

- Inertia-effects non-observable for times t >> $\tau_B$ so that d**v**/dt ≈ 0

$$\boxed{\mathbf{v}(t) = \frac{1}{\zeta_0}\mathbf{F}(t) \equiv \mathbf{v}^B(t)} \qquad (\Delta t \gg \tau_{\mathbf{B}}\ \ \&\ \ \Delta x \gg \sqrt{D_0 \tau_B})$$

Gaussian & Markovian (i.e. local in time) random velocity

$$\langle v_\alpha^B(t)\rangle = 0$$

$$\langle v_\alpha^B(t)\, v_\beta^B(t')\rangle = 2\, D_0\, \delta_{\alpha\beta}\, \delta(t - t')$$

white additive noise

$$\phi_v(t) = 2\, D_0\, \delta(t)$$

# Overdamped (positional) Langevin equation for a single free particle

$$\mathbf{r}(t)-\mathbf{r}_0=\int_0^t dt'\,\mathbf{v}^B(t')\equiv\Delta\mathbf{r}^B(t)$$

$$\left\langle \Delta\mathbf{r}^B(t)\right\rangle=0$$

$$\left\langle \Delta\mathbf{r}^B(t)\,\Delta\mathbf{r}^B(t)\right\rangle=2\,D_0\,\mathbf{1}\,\delta(t)$$

- $\Delta\mathbf{r}^B$ is Gaussian of zero mean and variance $2\,D_0\,\mathbf{1}\,\delta(t)$

$$(\mathbf{1})_{\alpha\beta}=\delta_{\alpha\beta}$$

$$\mathbf{u}\,\mathbf{w}:=\mathbf{u}\cdot\mathbf{w}^T$$

$$(\mathbf{u}\,\mathbf{w})_{\alpha\beta}=u_\alpha w_\beta$$

dyadic notation

$$P(\Delta\mathbf{r}^B,t)=(4\pi D_0 t)^{-3/2}\exp\left\{-\frac{(\Delta\mathbf{r}^B)^2}{4D_0 t}\right\}$$

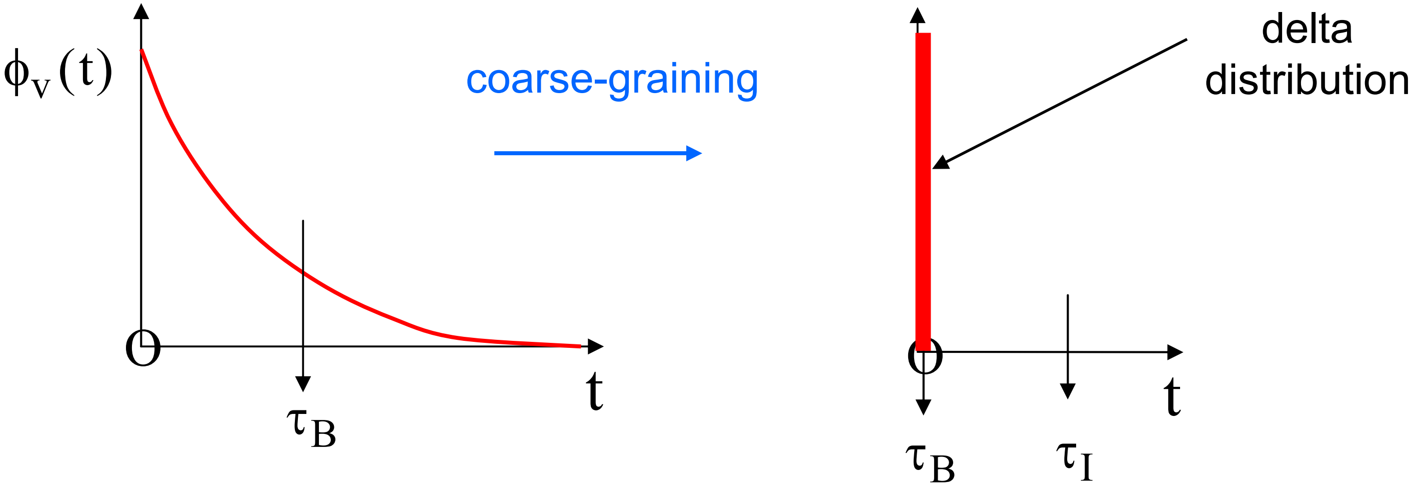
$$W(t)=\left\langle(\Delta\mathbf{r}^B)^2\right\rangle/6=D_0 t$$

MSD for t >> $\tau_B$

$$\boxed{\frac{\partial}{\partial t}P(\Delta\mathbf{r}^B,t)=D_0\,\nabla^2P(\Delta\mathbf{r}^B,t)}$$

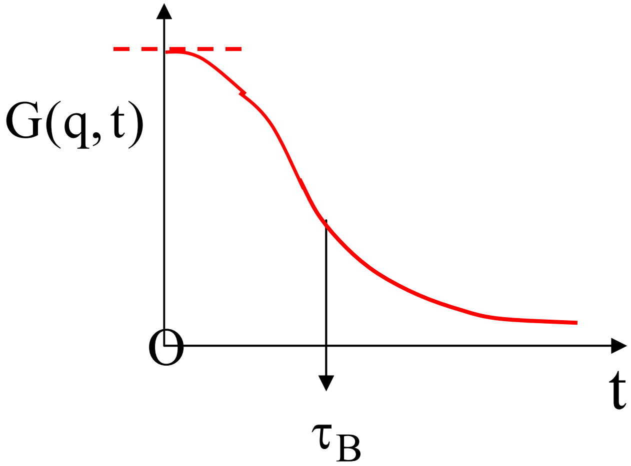
Smoluchowski eq. for free particle
statistically equiv. to positional Langevin eq.

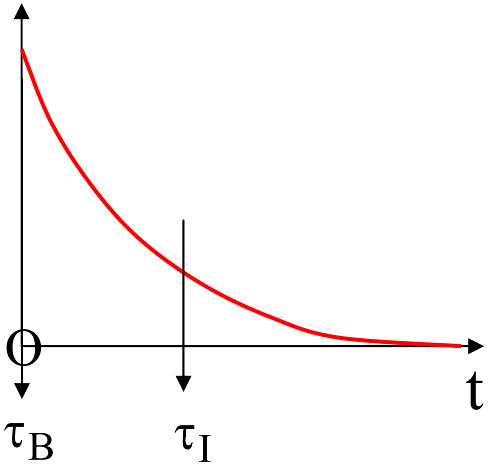
$$G(q,t)=\int d(\Delta\mathbf{r}^B)e^{i\mathbf{q}\cdot\Delta\mathbf{r}^B}\,P(\Delta\mathbf{r}^B,t)=e^{-q^2D_0t}$$



- Green-Kubo relation for free particle :

$$\boxed{D_0 = \int_0^\infty dt\, \phi_v(t)}$$

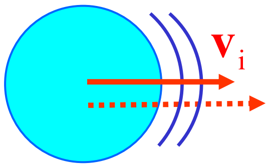




# Retarded free particle Langevin equation

$$M\frac{d}{dt}\mathbf{v}(t) = -\int_{-\infty}^{t} du\,\gamma(t-u)\,\mathbf{v}(u) + \mathbf{F}^{R}(t) \qquad (t \gg \tau_s)$$

Retarded solvent response



$\mathbf{F}_i = -\mathbf{F}_i^{H}$

Friction force on sphere
by surrounding solvent

$$\left\langle F_\alpha^R(t) \right\rangle_F = 0$$

$$\left\langle F_\alpha^R(t)\, F_\beta^R(t') \right\rangle_F = k_B T\, \delta_{\alpha\beta}\, \gamma(|t-t'|)$$

Gaussian & non-Markovian random force

- $\gamma(t)$ from linearized Navier-Stokes equation of incompressible fluid

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

$$\nabla \cdot \mathbf{u}(\mathbf{r},t) = 0 \qquad (t \gg \tau_c = a/c \approx 10^{-10}\ \text{sec})$$

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

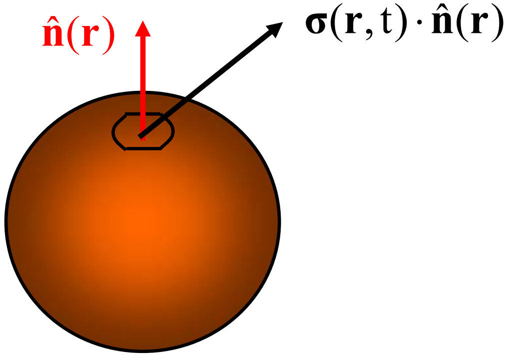
$$\text{Re} = \frac{\text{inertial force}}{\text{viscous force}} = \frac{\rho_s \sigma v_{th}}{\eta_0} \ll 1$$

$$\rho_s \frac{\partial \mathbf{u}(\mathbf{r},t)}{\partial t} = \nabla \cdot \boldsymbol{\sigma}(\mathbf{r},t)$$

$\boldsymbol{\sigma}(\mathbf{r},t)$ : Stress tensor of incompr. Newtonian fluid

$$\mathbf{F}^{H}(t)=\int_{S} dS\,\underbrace{\boldsymbol{\sigma}(\mathbf{r},t)\cdot\hat{\mathbf{n}}(\mathbf{r})}$$

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



$$\mathbf{F}^{H}(t)=-\int_{-\infty}^{t} du\,\gamma(t-u)\,\mathbf{v}(u)$$

Stokes-Boussinesq solution

$$\boldsymbol{\omega}(\mathbf{q},t)=\frac{1}{2}\int d\mathbf{r}\; e^{i\mathbf{q}\cdot\mathbf{r}}\;\nabla\times\mathbf{u}(\mathbf{r},t)$$

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

$$\Delta\rightarrow -q^{2}$$

$$\frac{\partial}{\partial t}[\nabla\times\mathbf{u}(\mathbf{r},t)]=\frac{\eta_0}{\rho_s}\Delta[\nabla\times\mathbf{u}(\mathbf{r},t)]$$

vorticity (shear-wave) diffusion due to unsteady particle motion

$$\frac{\partial}{\partial t}\omega(\mathbf{q},t)=-\frac{\eta_0}{\rho_s}q^{2}\omega(\mathbf{q},t)$$

$q=a^{-1}$ $\rightarrow \omega(\mathbf{q},t)/\omega(\mathbf{q},0)=e^{-t/\tau_\eta}$

$$\tau_\eta=a^{2}\frac{\rho_s}{\eta_0}=\frac{9}{2}\left(\frac{\rho_s}{\rho_p}\right)\tau_B$$

viscous hydrodynamic relaxation time for unsteady particle disturbances

- Hydrodynamic long-time tails from Boussinesq solution for $t \simeq \tau_\eta$

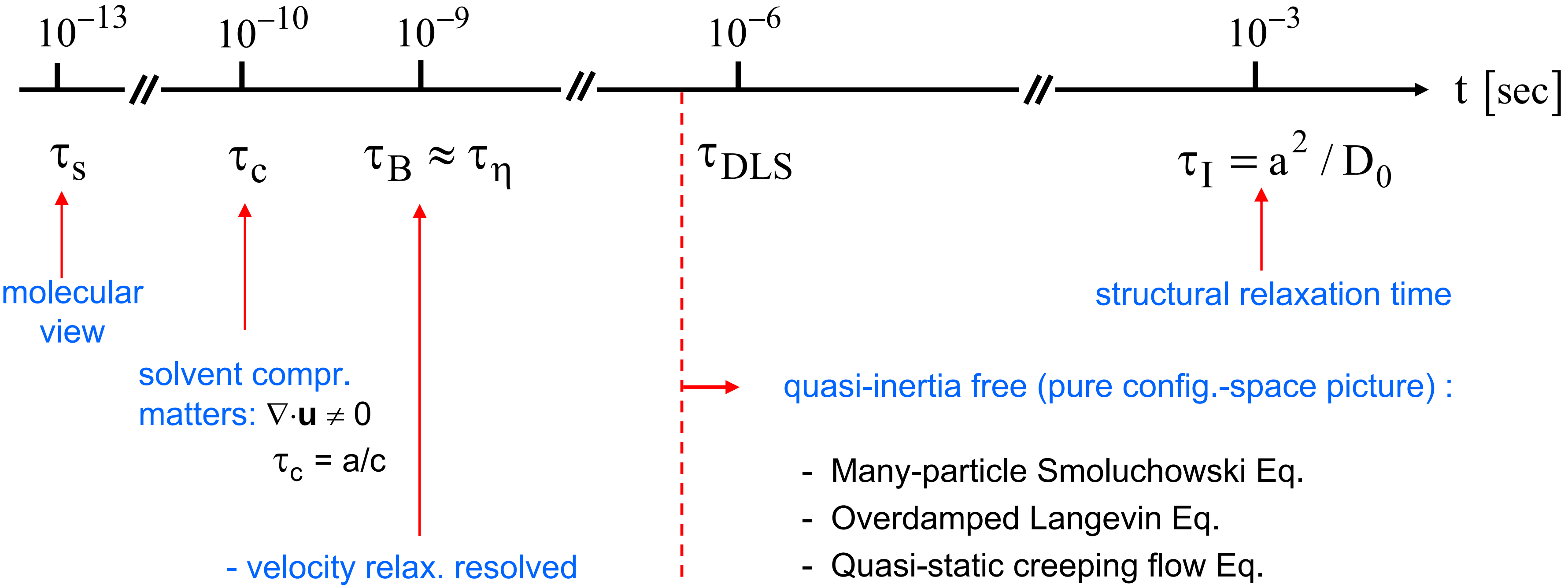
$$\phi_v(t) = \frac{d^2}{dt^2} W(t) \approx \frac{1}{9\sqrt{\pi}} \frac{k_B T}{M} \left( \frac{t}{\tau_\eta} \right)^{-3/2}$$

$$W(t) \approx D_0 t \left[ 1 - \frac{2}{\sqrt{\pi}} \left( \frac{t}{\tau_\eta} \right)^{-1/2} \right] \to D_0 t$$

Tail resolvable using DLS for micron-sized spheres

- Non-retarded Langevin-eq. applicable to colloids only for $t \gg \tau_B \approx \tau_\eta$
- Non-retarded Langevin-eq. applicable to aerosols for $t \simeq \tau_B \gg \tau_\eta$

# Colloidal time scales



molecular view

solvent compr. matters: $\nabla \cdot \mathbf{u} \neq 0$

$\tau_c = a/c$

- velocity relax. resolved
- unsteady solvent flow:
- retarded HI $\partial/\partial t\, \mathbf{u} \neq 0$

structural relaxation time

quasi-inertia free (pure config.-space picture) :

- Many-particle Smoluchowski Eq.
- Overdamped Langevin Eq.
- Quasi-static creeping flow Eq.

---

$\tau_B = M / \zeta_0$ transl. momentum relaxation time $(\zeta_0 = 6\pi\eta_0 a)$

$\tau_\eta = a^2 \rho_s / \eta_0 = 4.5 \left( \rho_s / \rho_p \right) \tau_B$ viscous relaxation time (vorticity diffusion)

(for aerosols: $\tau_\eta \ll \tau_B \Rightarrow$ non-retarded Langevin-eq. for $t \sim \tau_B$ )

Interacting particles: $a \to \xi(\phi, \ldots)$ (interaction/correlation length)

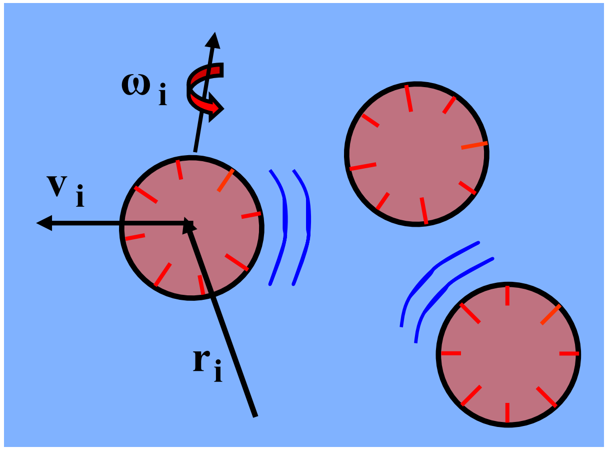
# Generalized Smoluchowski diffusion equation for dense systems

- N torque-free colloidal spheres in unbounded and quiescent (!) solvent
- Assume spherically symmetric direct pair interactions u(r)

→ translational degrees of freedom decouple from rotational ones

Probability conservation of configurational Pdf :

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



Quasi-inertia free motion for $t \gg \tau_B \approx \tau_\eta$

total force on i $= \ \mathbf{0} \ = \mathbf{F}_i^p + \mathbf{F}_i^{ex} + \mathbf{F}_i^H + \mathbf{F}_i^B$

---

$$\mathbf{F}_i^p = -\nabla_i U(\mathbf{r}^N) = -\sum_{l=1}^{N}{}' \nabla_i\, u(r_{il})$$ direct forces

$$\mathbf{F}_i^{ex} = -\nabla_i U^{ex}(\mathbf{r}^N)$$ external forces (e.g. gravity)

$$\mathbf{F}_i^H = -\sum_{l=1}^{N} \zeta_{il}(\mathbf{r}^N) \cdot \mathbf{v}_l$$ hydrodyn. force on i (by surrounding fluid)

$$\mathbf{F}_i^B = -k_B T\, \nabla_i \ln P$$ Brownian force (drives diffusion)

Solve for the $\mathbf{v}_i$ using generalized hydrodynamic Stokes-Einstein relation :

$$\sum_{l=1}^{N} \zeta_{il}(\mathbf{r}^N)\cdot\mathbf{D}_{lj}(\mathbf{r}^N) = k_B T\,\delta_{ij}\,\mathbf{1} \qquad \zeta(X)\cdot\mathbf{D}(X) = k_B T\,\mathbf{1} \qquad (X=\mathbf{r}^N)$$

real, symmetric + pos. definite 3N x 3N matrix

$$\mathbf{v}_i = -\beta\sum_{l=1}^{N}\mathbf{D}_{il}(\mathbf{r}^N)\cdot\left[\mathbf{F}_l^H = -\mathbf{F}_l^p - \mathbf{F}_l^{ex} - \mathbf{F}_l^B\right] = \sum_{l=1}^{N}\mathbf{D}_{il}(\mathbf{r}^N)\cdot\left[\beta\,\mathbf{F}_l^p + \beta\,\mathbf{F}_l^{ex} - \nabla_l \ln P(\mathbf{r}^N,t)\right]$$

Insertion in continuity eq. leads to generalized Smoluchowski equation (GSE) :

$$\boxed{\frac{\partial}{\partial t}P(\mathbf{r}^N,t) = \hat{O}(\mathbf{r}^N)P(\mathbf{r}^N,t)} \qquad \boxed{\hat{O}(\mathbf{r}^N) = \sum_{i,j=1}^{N}\nabla_i\cdot\mathbf{D}_{ij}\cdot\left[\nabla_j - \beta\left(\mathbf{F}_j^p + \mathbf{F}_j^{ex}\right)\right]}$$

Smoluchowski differential operator

Choice of Brownian forces was such that :

$$\hat{O}(\mathbf{r}^N)e^{-\beta\left[U+U^{ex}\right]} = 0 \quad \text{i.e.} \quad e^{-\beta\left[U+U^{ex}\right]} \quad \text{is stationary solution}$$

$$P(\mathbf{r}^N,t)\to P_{eq}(\mathbf{r}^N)\propto e^{-\beta U} \qquad (t\to\infty\ \&\ U^{ex}=0)$$

H-theorem of
Smoluchowski dynamics

For hydrodynamically non-interacting spheres is :

$\mathbf{D}_{ij}(\mathbf{r}^N) = D_0\delta_{ij}\mathbf{1}$ i.e. $\mathbf{v}_i = -\sum_{l=1}^{N}\underbrace{\beta\,\mathbf{D}_{il}(\mathbf{r}^N)}\cdot\mathbf{F}_l^H \to -\beta\,D_0\,\mathbf{F}_i^H$

$$\hat{O}(\mathbf{r}^N) = D_0\sum_{i=1}^{N}\nabla_i\cdot\left[\nabla_i - \beta\left(\mathbf{F}_i^p + \mathbf{F}_i^{ex}\right)\right]$$

Translational-translational (tt) hydrodynamic mobilities
(linear velocity-force relations implied by linearity of hydrodyn. eqs. for fluid motion)

For totally non-interacting spheres is :

$$\hat{O}_0(\mathbf{r}^N) = D_0\sum_{i=1}^{N}\nabla_i^2$$

→ (sum of) single-particle diffusion equations

# Irreversibility of overdamped Brownian dynamics („H-Theorem“)

$$P_{eq}(\mathbf{r}^N) = \frac{e^{-\beta U(\mathbf{r}^N)}}{\int d\mathbf{x}^N e^{-\beta U(\mathbf{x}^N)}} = \frac{e^{-\beta U(\mathbf{r}^N)}}{Z}$$

equilibrium Pdf ; $U^{ex} = 0$

Consider free-energy-type functional A[P] on solution space of GSE defined by

$$A([P],t) = \int d\mathbf{r}^N\, P(\mathbf{r}^N,t)\left[k_B T \,\ln P + U\right] \longrightarrow A[P_{eq}] = -k_B T\,\ln Z$$

$$\frac{dA}{dt} = \int d\mathbf{r}^N \left\{ \frac{\partial P}{\partial t}\left[k_B T\,\ln P + U\right] + k_B T\,\frac{\partial P}{\partial t} \right\}$$

$$\frac{dA}{dt} = \int d\mathbf{r}^N \left\{ \sum_{i,j} \nabla_i \cdot \mathbf{D}_{ij} \cdot \underbrace{\left(\nabla_j P + \beta P \nabla_j U\right)}_{P\nabla_j \ln(P/P_{eq})} \left[k_B T\,\ln P + U\right] + k_B T \sum_{i,j} \nabla_i \cdot \mathbf{D}_{ij} \cdot \underbrace{\left(\nabla_j P + \beta P \nabla_j U\right)}_{P\nabla_j \ln(P/P_{eq})} \right\}$$

Integrate by parts : surface terms vanish for P = 0 and grad P = 0 on system boundaries (zero flux)

$$\frac{dA}{dt} = -k_B T \int d\mathbf{r}^N\, P \left\{ \sum_{i,j} \left[\nabla_i \ln(P/P_{eq})\right] \cdot \mathbf{D}_{ij} \cdot \left[\nabla_j \ln(P/P_{eq})\right] \right\} < 0$$

$$\mathbf{D}_{ij} = \mathbf{D}_{ji}$$

$$\sum_{i\,j} \mathbf{D}_{ij} : \mathbf{f}_i^* \mathbf{f}_j > 0$$

A([P],t) decays monotonically in time until its minimum A[Peq] is reached where dA/dt = 0

## More „fundamental“ derivations of GSE :

- Murphy & Aguirre, J. Chem. Phys. (1972) : from many-sphere Fokker-Planck eq.

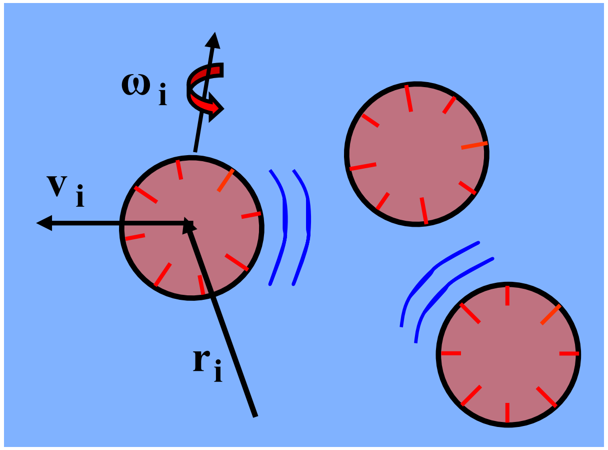
- Roux, Physica A (1992) : from fluctuating hydrodynamics

# 5. Hydrodynamic mobility problem of many spheres

- General properties of hydrodynamic interaction
- Method of induced forces
- Motion along a liquid-gas interface

# General properties of hydrodynamic interaction

- Hydrodynamic mobility tensors in GSE follow from associated creeping flow BV problem
- Quasi-stationary fluid flow for $t \gg \tau_\eta \approx \tau_B$



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

Linear Stokes‘ eq.
for fluid flow field
(zero total force density)

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

Incompressibility of fluid

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

Stress tensor

$$\mathbf{u}(\mathbf{r}) = \mathbf{v}_i + \boldsymbol{\omega}_i \times (\mathbf{r} - \mathbf{r}_i)$$

for **r** on sphere surface $S_i$ (stick inner BC)

$$\mathbf{u}(\mathbf{r}) \to 0 \, , \; |\mathbf{r}| \to \infty$$

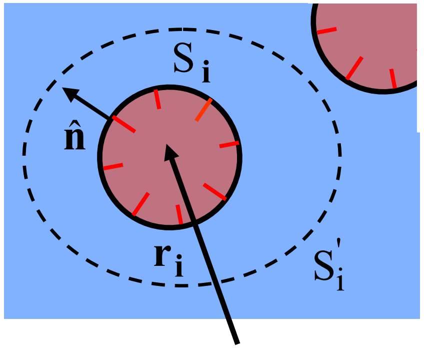
outer BC for quiescent and unbound fluid

---

**Helmholtz (1868) :**

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

- Hydrodynamic force and torque on surface of sphere i



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

$$\mathbf{T}_i^H = \int_{S_i} dS\, (\mathbf{r}-\mathbf{r}_i)\times\boldsymbol{\sigma}(\mathbf{r};\mathbf{r}^N)\cdot\hat{\mathbf{n}}(\mathbf{r})$$

- Forces and torques are transmitted through fluid since div $\boldsymbol{\sigma}$ = 0 <u>within</u> fluid

- Friction problem for quiescent fluid: linearity of Stokes flow implies that :

$$\begin{pmatrix}\mathbf{F}^H\\ \mathbf{T}^H\end{pmatrix} = -\underbrace{\begin{pmatrix}\zeta^{tt}(X) & \zeta^{tr}(X)\\ \zeta^{rt}(X) & \zeta^{rr}(X)\end{pmatrix}}_{\text{3N x 3N each, depend only on X}}\cdot\begin{pmatrix}\mathbf{v}\\ \boldsymbol{\omega}\end{pmatrix} \longleftarrow$$

Supervector / -matrix notation :

$\mathbf{v} = (\mathbf{v}_1,\ldots,\mathbf{v}_N)^T$ et cetera

- Torque-free spheres: **T**$^H$ = 0 → eleminate $\boldsymbol{\omega}$ in favor of **v**

$$\mathbf{F}^H = -\underbrace{\left[\zeta^{tt}-\zeta^{tr}\cdot(\zeta^{rr})^{-1}\cdot\zeta^{rt}\right]}_{=:\,\zeta(X)}\cdot\mathbf{v}$$

- Relate to inverse mobility problem since mobilities needed as input in GSE

$$\begin{pmatrix} \mathbf{v} \\ \boldsymbol{\omega} \end{pmatrix} = -\beta \begin{pmatrix} \mathbf{D}^{tt}(X) & \mathbf{D}^{tr}(X) \\ \mathbf{D}^{rt}(X) & \mathbf{D}^{rr}(X) \end{pmatrix} \cdot \begin{pmatrix} \mathbf{F}^{H} \\ \mathbf{T}^{H} = 0 \end{pmatrix} \longrightarrow \mathbf{v} = -\beta\, \mathbf{D}^{tt}(X) \cdot \mathbf{F}^{H}$$

- Solving the hydrodynamic Stokes-Einstein relation for $\mathbf{D}^{tt}$ gives

$$\underbrace{\begin{pmatrix} \zeta^{tt} & \zeta^{tr} \\ \zeta^{rt} & \zeta^{rr} \end{pmatrix}} \cdot \underbrace{\begin{pmatrix} \mathbf{D}^{tt} & \mathbf{D}^{tr} \\ \mathbf{D}^{rt} & \mathbf{D}^{rr} \end{pmatrix}} = k_B T \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}$$

symmetric & positive definite 6N x 6N matrices

$$\mathbf{D}(X) = \mathbf{D}^{tt}(X) = k_B T \left[ \zeta^{tt} - \zeta^{tr} \cdot (\zeta^{rr})^{-1} \cdot \zeta^{rt} \right]^{-1} = k_B T\, \boldsymbol{\zeta}(X)^{-1} \longrightarrow \text{GSE}$$

- Symmetry follows from Lorentz‘ reciprocal theorem of Stokes flow or Green-Kubo form of **D**

$$\longrightarrow \quad \mathbf{D}^{tt}_{ij} = \mathbf{D}^{tt}_{ji} \qquad \mathbf{D}^{rr}_{ij} = \mathbf{D}^{rr}_{ji} \qquad \mathbf{D}^{rt}_{ij} = \mathbf{D}^{tr}_{ji}$$

- Without hydrodynamic interactions (very dilute system) is :

$$\mathbf{D}_{ij}^{tt} = D_0\,\delta_{ij}\mathbf{1} \qquad \mathbf{D}_{ij}^{rr} = \mathbf{D}_0^{r}\,\delta_{ij}\mathbf{1} \qquad \mathbf{D}_{ij}^{rt} = \mathbf{0} = \mathbf{D}_{ij}^{tr}$$

$$\boxed{D_0 = \frac{k_B T}{6\pi\eta_0 a}} \qquad \mathbf{F}_i^{H} = -6\pi\eta_0 a\,\mathbf{v}_i$$

(6 → 4 : perfect slip)

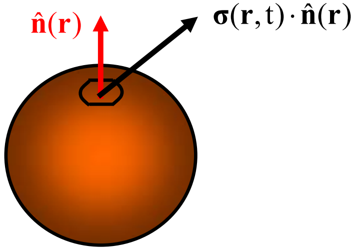
$$\boxed{D_0^{r} = \frac{k_B T}{8\pi\eta_0 a^3}} \qquad \mathbf{T}_i^{H} = -8\pi\eta_0 a^3\,\boldsymbol{\omega}_i$$

(8 → 0 : perfect slip)

# Positive definiteness of hydrodynamic mobility matrices

- Rate of heat-dissipated energy created by sphere‘s motion relative to fluid :

$$\frac{dE}{dt} = \sum_{i=1}^{N} \int_{S_i} dS\, \mathbf{u}(\mathbf{r}) \cdot \underbrace{\left[-\boldsymbol{\sigma}(\mathbf{r}) \cdot \hat{\mathbf{n}}(\mathbf{r})\right]} > 0$$



$\mathbf{v}_i + \boldsymbol{\omega}_i \times (\mathbf{r} - \mathbf{r}_i)$

force/area on fluid caused by surface element dS

$$\frac{dE}{dt} = -\sum_{i=1}^{N} \left[\mathbf{v}_i \cdot \mathbf{F}_i^H + \boldsymbol{\omega}_i \cdot \mathbf{T}_i^H\right] = (\mathbf{v}, \boldsymbol{\omega}) \cdot \begin{pmatrix} \zeta^{tt} & \zeta^{tr} \\ \zeta^{rt} & \zeta^{rr} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{v} \\ \boldsymbol{\omega} \end{pmatrix} = \beta\left(\mathbf{F}^H, \mathbf{T}^H\right) \cdot \begin{pmatrix} \mathbf{D}^{tt} & \mathbf{D}^{tr} \\ \mathbf{D}^{rt} & \mathbf{D}^{rr} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{F}^H \\ \mathbf{T}^H \end{pmatrix} > 0$$

- v and $\omega$ can be chosen arbitrarily : $\mathbf{D}^{tt}(X)$ and $\mathbf{D}^{rr}(X)$ positive definite

- From Stokes equation follows additionally that, with : $\mathbf{e}(\mathbf{r}) = \left[\nabla\mathbf{u} + (\nabla\mathbf{u})^T\right]/2$

rate of strain tensor

$$\frac{dE}{dt} = 2\eta_0 \int_V d\mathbf{r}\, \mathbf{e}(\mathbf{r}) : \mathbf{e}(\mathbf{r}) = 2\eta_0 \int_V d\mathbf{r} \sum_{\alpha,\beta=1}^{3} \left(e_{\alpha\beta}\right)^2 > 0$$

# Point-force solution

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

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

volumetric force density on fluid

- The solution for outer BC **u**(**r** → ∞) = 0 and p(**r** → ∞) = 0 is :

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

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

Oseen tensor

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

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

including **r** = 0

- Superposition gives flow-field due to N pointlike particles at positions { $\mathbf{r}_i$ } :

$$\mathbf{f}(\mathbf{r}') = -\sum_{i=1}^{N} \mathbf{F}_i^H \delta(\mathbf{r}' - \mathbf{r}_i) \longrightarrow \mathbf{u}(\mathbf{r}) = \int d\mathbf{r}'\,\mathbf{T}_0(\mathbf{r} - \mathbf{r}') \cdot \mathbf{f}(\mathbf{r}') = -\sum_{i=1}^{N} \mathbf{T}_0(\mathbf{r} - \mathbf{r}_i) \cdot \mathbf{F}_i^H$$

fluid force on particle i

- Assume stick BC: particles move with same velocity as fluid in contact, i.e. $\mathbf{u}(\mathbf{r}_i) = \mathbf{v}_i$

- To avoid unphysical divergence (drawback of pointforce appr.) assume pointforce solution for particle i to describe additional velocity change due to (N - 1) particles - HI alone :

$$\mathbf{v}_i \approx \mathbf{v}_i^0 + \Delta\mathbf{v}_i^{(N-1)}$$

$$\mathbf{v}_i^0 = -\beta\, D_0\, \mathbf{F}_i^H \qquad \left( D_0 = \frac{k_B T}{6\pi\eta_0 a} \right)$$

$$\Delta\mathbf{v}_i^{(N-1)} = -\sum_{l\neq i}^{N} \mathbf{T}_0(\mathbf{r}_i - \mathbf{r}_l)\cdot\mathbf{F}_l^H$$

assumed to be finite

- Comparison with gen. Stokes friction law for torque-free spheres identifies mobilities as:

$$\mathbf{v}_i = -\sum_{l=1}^{N} \beta\, \mathbf{D}_{il}(\mathbf{r}^N)\cdot\mathbf{F}_l^H \quad \Rightarrow \quad \mathbf{D}_{ii}(\mathbf{r}^N) = D_0 \mathbf{1}$$

$$\mathbf{D}_{ij}(\mathbf{r}^N) = k_B T\, \mathbf{T}_0(\mathbf{r}_i - \mathbf{r}_j) = D_0 \frac{3a}{4 r_{ij}}\left[\mathbf{1} + \hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij}\right] \quad (i \neq j)$$

valid up to $O(a^2/r^2)$

- Real justification follows from considering finite-sized spheres of radius a

# Derivation of fundamental solution (Oseen tensor) for unbounded fluid

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

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

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

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

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

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

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

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

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

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

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

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

# Point-force solution

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

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

volumetric force density on fluid

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Oseen tensor

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including **r** = 0

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$$\mathbf{v}_i^0 = -\beta\, D_0\, \mathbf{F}_i^H \qquad (D_0 = \frac{k_B T}{6\pi\eta_0 a})$$

$$\Delta\mathbf{v}_i^{(N-1)} = -\sum_{l\neq i}^{N} \mathbf{T}_0(\mathbf{r}_i - \mathbf{r}_l)\cdot\mathbf{F}_l^H$$

assumed to be finite

- Comparison with gen. Stokes friction law for torque-free spheres identifies mobilities as:

$$\mathbf{v}_i = -\sum_{l=1}^{N} \beta\, \mathbf{D}_{il}(\mathbf{r}^N)\cdot\mathbf{F}_l^H \quad \Rightarrow$$

$$\mathbf{D}_{ii}(\mathbf{r}^N) = D_0 \mathbf{1}$$

$$\mathbf{D}_{ij}(\mathbf{r}^N) = k_B T\, \mathbf{T}_0(\mathbf{r}_i - \mathbf{r}_j) = D_0 \frac{3a}{4 r_{ij}}\left[\mathbf{1} + \hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij}\right] \quad (i \neq j)$$

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

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

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

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

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

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

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

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

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

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

- have employed that :

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

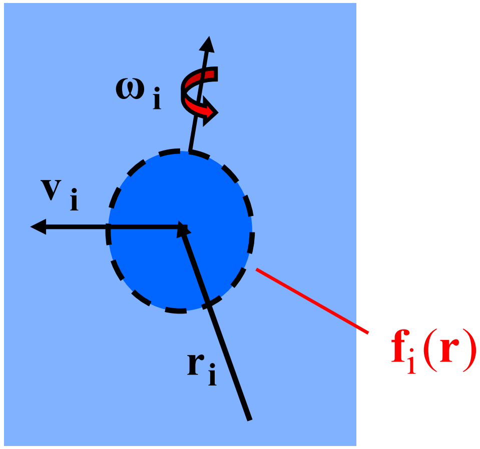
$$\int d\Omega_q\, e^{\pm i\mathbf{q}\cdot\mathbf{r}}\, \mathbf{1} = 4\pi\, j_0(q\, r)\, \mathbf{1}$$

$$\int d\Omega_q\, e^{\pm i\mathbf{q}\cdot\mathbf{r}}\, \hat{\mathbf{q}}\,\hat{\mathbf{q}} = 4\pi\left[\frac{j_1(q\, r)}{q\, r}\mathbf{1} - j_2(q\, r)\,\hat{\mathbf{r}}\,\hat{\mathbf{r}}\right] \qquad j_2(x) = \frac{3\, j_1(x)}{x} - j_0(x)$$

# Method of induced forces

- Replace spheres by fluid in rigid-body motion according to stick inner BCs
- Introduce config.-dependent induced force densities on fluid which enforce BCs
- BV problem identical to original one outside of spheres
- Assume incident flow field $\mathbf{u}_0$ (non-quiescent unbound fluid)

$$\mathbf{f}(\mathbf{r};X) = \sum_{i=1}^{N} \mathbf{f}_i(\mathbf{r}) \qquad \mathbf{f}_i(\mathbf{r}) = -\delta(|\mathbf{r}-\mathbf{r}_i|-a^+)\boldsymbol{\sigma}(\mathbf{r};X)\cdot\hat{\mathbf{n}}(\mathbf{r})$$



$$\mathbf{u}(\mathbf{r}) - \mathbf{u}_0(\mathbf{r}) = \int_{V_i^+} d\mathbf{r}'\, \mathbf{T}_0(\mathbf{r}-\mathbf{r}')\cdot\mathbf{f}_i(\mathbf{r}') + \sum_{l\neq i}^{N} \int_{V_l^+} d\mathbf{r}'\, \mathbf{T}_0(\mathbf{r}-\mathbf{r}')\cdot\mathbf{f}_l(\mathbf{r}')$$

$$\mathbf{u}(\mathbf{r}) = \mathbf{v}_i + \boldsymbol{\omega}_i \times (\mathbf{r}-\mathbf{r}_i)$$

(inside sphere i)

$$\mathbf{u}(\mathbf{r}\to\infty) = \mathbf{u}_0(\mathbf{r})$$

incident flow due to infinite distant forces / boundaries)

$$-\nabla p_0(\mathbf{r}) + \eta_0 \nabla^2 \mathbf{u}_0(\mathbf{r}) = 0 \qquad \nabla\cdot\mathbf{u}_0(\mathbf{r}) = 0$$ (homog. Stokes eq.) $\Rightarrow \Delta p_0(\mathbf{r}) = 0$

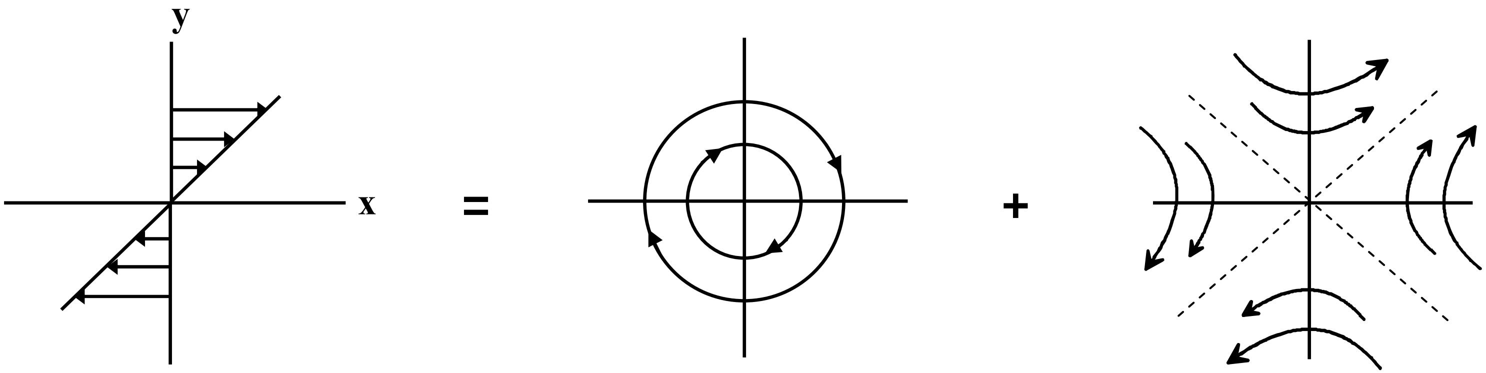
$$\Rightarrow \nabla^2\nabla^2\mathbf{u}_0(\mathbf{r}) = 0$$ (bi–harmonic → mean value property)

# Important example : simple linear shear flow

$$\mathbf{u}_0(\mathbf{r}) = \dot{\gamma}\,\boldsymbol{\Gamma}\cdot\mathbf{r} = \dot{\gamma}\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\cdot\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \boldsymbol{\omega}_0\times\mathbf{r} + \mathbf{e}_0 : \mathbf{r}$$

$$\boldsymbol{\omega}_0(\mathbf{r}) = \frac{1}{2}\nabla\times\mathbf{u}_0(\mathbf{r}) = \frac{1}{2}\dot{\gamma}\,\boldsymbol{\varepsilon}:\boldsymbol{\Gamma} = -\frac{1}{2}\dot{\gamma}\hat{\mathbf{z}}$$

$$\mathbf{e}_0(\mathbf{r}) = \frac{1}{2}\left[(\nabla\mathbf{u}_0)(\mathbf{r}) + (\nabla\mathbf{u}_0)^{\mathrm{T}}(\mathbf{r})\right] - \frac{1}{3}\mathrm{Tr}(\nabla\mathbf{u}_0(\mathbf{r})) = \frac{1}{2}\dot{\gamma}\left[\boldsymbol{\Gamma} + \boldsymbol{\Gamma}^{\mathrm{T}}\right]$$



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

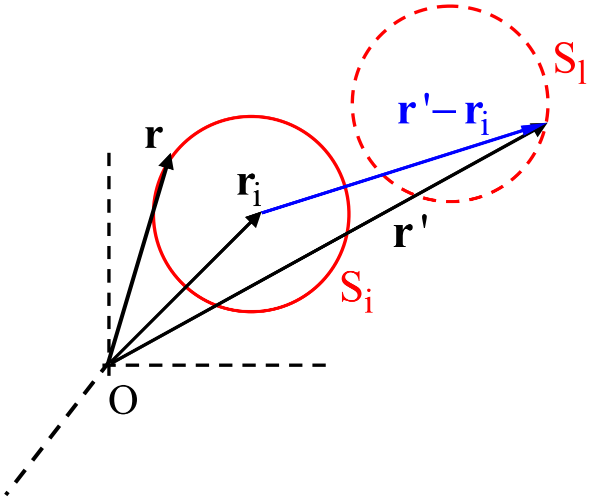
# Mean-value property of bi-harmonic functions

$$\nabla \cdot \mathbf{u}_0(\mathbf{x}) = 0 \qquad \nabla^2\nabla^2\mathbf{u}_0(\mathbf{x}) = 0$$

$$\nabla \cdot \mathbf{T}_0(\mathbf{x}) = 0 \qquad \nabla^2\nabla^2\mathbf{T}_0(\mathbf{x}) = 0 \qquad (\text{all } \mathbf{x})$$

$$\left\langle \mathbf{u}_0(\mathbf{r}) \right\rangle_{S_i} \equiv \frac{1}{4\pi a^2}\int_{S_i} dS\, \mathbf{u}_0(\mathbf{r}) = \mathbf{u}_0(\mathbf{r}_i) + \frac{a^2}{6}\left(\nabla^2\mathbf{u}_0\right)(\mathbf{r}_i)$$

$$\frac{1}{4\pi a^2}\int_{S_i} dS\, \mathbf{T}_0(\mathbf{r}-\mathbf{r}') = \begin{cases} \left(\mathbf{1} + \frac{a^2}{6}\nabla^2\right)\mathbf{T}_0(\mathbf{r}'-\mathbf{r}_i) & |\mathbf{r}'-\mathbf{r}_i| \geq a \\ \frac{1}{6\pi\eta_0 a}\mathbf{1} & |\mathbf{r}'-\mathbf{r}_i| \leq a \end{cases}$$



## „Proof“ of mean-value theorem by Taylor expansion around center of sphere i :

$$\mathbf{u}_0(\mathbf{r}) = \sum_{n=0}^{\infty} \frac{(\mathbf{r}-\mathbf{r}_i)^n \odot \nabla^n}{n!} \mathbf{u}_0(\mathbf{r})\Big|_{\mathbf{r}=\mathbf{r}_i} = \mathbf{u}_0(\mathbf{r}_i) + (\mathbf{r}-\mathbf{r}_i)\cdot\nabla\mathbf{u}_0(\mathbf{r}_i) + \frac{1}{2}(\mathbf{r}-\mathbf{r}_i)(\mathbf{r}-\mathbf{r}_i):\nabla\nabla\mathbf{u}_0(\mathbf{r}_i) + \ldots$$

$$\nabla^2\nabla^2\mathbf{u}_0 = 0 \qquad \nabla\cdot\mathbf{u}_0 = 0$$

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

$$\Longrightarrow$$

$$\int_{S_i} dS\,\mathbf{u}_0(\mathbf{r}) = 4\pi a^2 \mathbf{u}_0(\mathbf{r}_i) + 0 + \underbrace{\left(\frac{1}{2}\int_{S_i} dS\,\mathbf{x}\,\mathbf{x}\right)}_{\frac{4\pi}{6}a^4\mathbf{1}} : \nabla\nabla\mathbf{u}_0(\mathbf{r}_i) + 0$$

$$\int_{S_i} dS\,\mathbf{u}_0(\mathbf{r}) = 4\pi a^2 \left(\mathbf{1} + \frac{a^2}{6}\nabla^2\right)\mathbf{u}_0(\mathbf{r}_i)$$

- Integrate induced-force eq. over surface of singled out sphere i w/r to **r**

- Use mean-value properties and :

$$\int_{S_i^+} dS\, \mathbf{u}(\mathbf{r}) = \int_{S_i^+} dS\, \left[\mathbf{v}_i + \boldsymbol{\omega} \times \left(\mathbf{r} - \mathbf{r}_i\right)\right] = 4\pi a^2 \mathbf{v}_i$$

$$\mathbf{F}_i^H = -\int_{V_i^+} d\mathbf{r}'\, \mathbf{f}_i(\mathbf{r}')$$

---

- Leads to exact result for hydrodynamic force on sphere i :

$$\mathbf{F}_i^H = -6\pi\eta_0 a\left[\mathbf{v}_i - \left(\mathbf{1} + \frac{a^2}{6}\nabla_i^2\right)\left(\mathbf{u}_{N-1}(\mathbf{r}_i;X) + \mathbf{u}_0(\mathbf{r}_i)\right)\right]$$

generalized translational
Faxén law (stick BC)

$$\mathbf{u}_{N-1}(\mathbf{r}_i;X) = \sum_{l\neq i}^{N} \int_{V_l^+} d\mathbf{r}'\, \mathbf{T}_0(\mathbf{r}-\mathbf{r}')\cdot \mathbf{f}_l(\mathbf{r}',X)$$

Flow part due to N -1 spheres except sphere i
But: $\mathbf{f}_l$ fullfills full N - sphere stick BCs

# Applications of generalized Faxén law

$$\mathbf{F}_i^H = -6\pi\eta_0 a \left[ \mathbf{v}_i - \left( \mathbf{1} + \frac{a^2}{6}\nabla^2 \right) \mathbf{u}_0(\mathbf{r} = \mathbf{r}_i) \right]$$

- Single-sphere Faxén law
- Stokes friction law when $\mathbf{u}_0 = 0$

$$\mathbf{f}_i(\mathbf{r};X) \rightarrow -\mathbf{F}_i^H \delta(\mathbf{r} - \mathbf{r}_i) \qquad 6\pi\eta_0 a \rightarrow \zeta_0$$

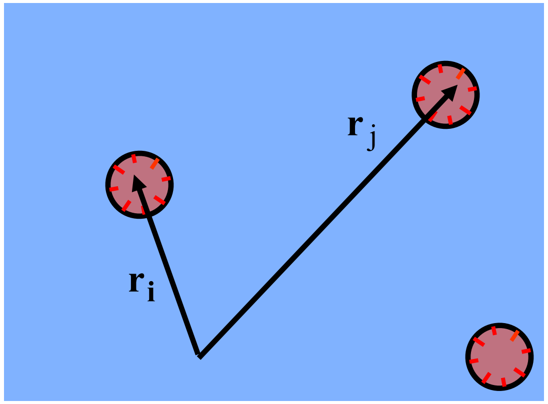
$$\mathbf{v}_i - \mathbf{u}_0(\mathbf{r}_i) = -\frac{1}{\zeta_0}\mathbf{F}_i^H - \sum_{l \neq i}^{N} \mathbf{T}_0(\mathbf{r}_i - \mathbf{r}_l) \cdot \mathbf{F}_l^H$$

- Point-particle limit with incident flow

- Dilute suspension where : $|\mathbf{r}_i - \mathbf{r}_j| \gg a\,,\quad \mathbf{f}_l(\mathbf{r}') \rightarrow -\mathbf{F}_l^H / V_{sp}$

Expand $\mathbf{T}_0(\mathbf{r}' - \mathbf{r}_i)$ around $|\mathbf{r}_l - \mathbf{r}_i|$ to leading order

Use that : $\nabla^2 \mathbf{T}_0(\mathbf{r}) = \dfrac{1}{4\pi\eta_0 r^3}[\mathbf{1} - 3\hat{\mathbf{r}}\hat{\mathbf{r}}]$



leads to Rotne – Prager approximation for t - t mobilities :

$$\mathbf{v}_i - \langle \mathbf{u}_0(\mathbf{r}) \rangle_{S_i} = -\beta \sum_{l=1}^{N} \underbrace{D_0 \{\mathbf{1}\delta_{il} + (1-\delta_{il})\mathbf{T}_{RP}(\mathbf{r}_l - \mathbf{r}_i)\}} \cdot \mathbf{F}_l^H$$

$$\boxed{\mathbf{D}_{il}(\mathbf{r}^N) \approx \mathbf{D}_{il}^{RP}(\mathbf{r}_{il})}$$

$$\mathbf{T}_{RP}(\mathbf{r}) = \zeta_0 \left( \mathbf{1} + 2 \cdot \frac{a^2}{6} \nabla^2 \right) \mathbf{T}_0(\mathbf{r}) = \frac{3}{4}\left(\frac{a}{r}\right)(\mathbf{1} + \hat{\mathbf{r}}\hat{\mathbf{r}}) + \frac{1}{2}\left(\frac{a}{r}\right)^3 (\mathbf{1} - 3\hat{\mathbf{r}}\hat{\mathbf{r}})$$

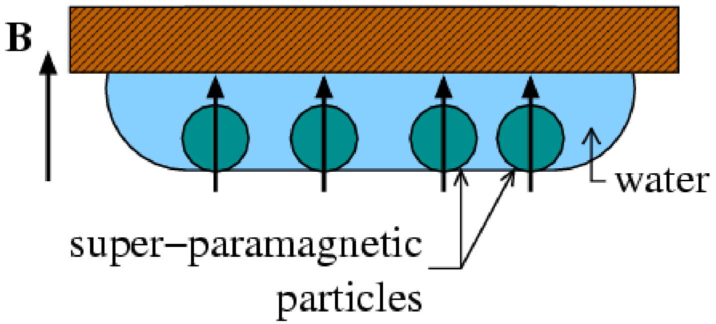
Note that in Rotne – Prager approximation is :

- HI pairwise additive
- Neglect of reflections

$$\nabla_i \cdot D_{RP}(\mathbf{r}_{il}) = 0$$

➡ Multipole expansions including reflections & more-body HI

# Motion along a liquid-gas interface



# Calculation of hydrodynamic quasi-2D mobilities :

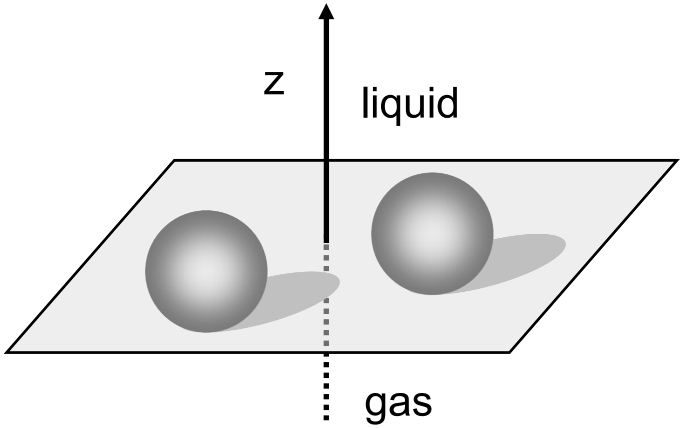
→ assume ideally flat and thin interface (valid to very good accuracy)

→ spheres touch interface in single point; only lateral motion

→ creeping flow :

$$\eta_0 \Delta \mathbf{u}(\mathbf{r}) - \nabla p(\mathbf{r}) = 0 \ , \quad \nabla \cdot \mathbf{u}(\mathbf{r}) = 0 \qquad (\mathbf{r} \in V_{\mathrm{liq}})$$

$$\mathbf{u}(\mathbf{r}) = \mathbf{V}_i + \mathbf{\Omega}_i \times \left(\mathbf{r} - \mathbf{r}_i\right) \ , \quad (\mathbf{r} \in S_i , \ \text{stick BC})$$



Free surface BC´s :

$$u_z(\mathbf{r})\big|_{z=0} = 0$$

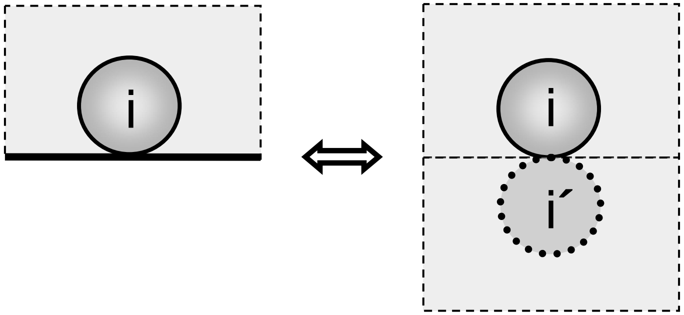
$$\boldsymbol{\sigma}_{xz}(\mathbf{r})\big|_{z=0} = 0 = \boldsymbol{\sigma}_{yz}(\mathbf{r})\big|_{z=0}$$

(zero tangential stress)

( Cichocki, Ekiel-Jezewska, G.N., Waijnryb, JCP 121 & Europhys. Lett. 67 (2004) )

- Free surface BC´s accounted for by method of images

real:
N-sphere system



fictitious:
unbounded 2N-sphere system

$$\mathbf{u}(\mathbf{r}) - \mathbf{u}_0(\mathbf{r}) = \sum_{j=1}^{N} \int d\bar{\mathbf{r}} \left\{ \mathbf{T}_0(\mathbf{r}-\bar{\mathbf{r}}) + \mathbf{T}_0(\mathbf{r}-\bar{\mathbf{r}}') \cdot \left(\mathbf{1} - 2\,\hat{\mathbf{z}}\hat{\mathbf{z}}\right) \right\} \cdot \mathbf{f}_j(\bar{\mathbf{r}})$$

incident flow
(+ reflection)

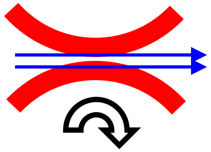
3D Oseen tensor

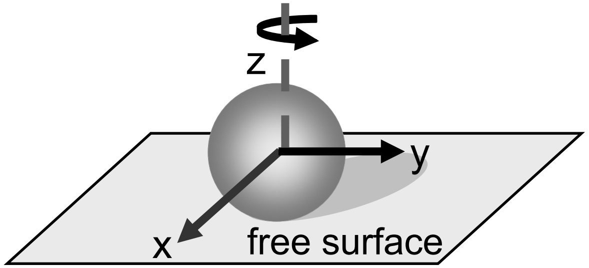
reflection at z=0

force density on $S_j$

- Only 3 degrees of freedom due to lubrication

$$V_{iz} = 0$$
$$\Omega_{ix} = \Omega_{iy} = 0$$





$$\begin{pmatrix} V_{1x} \\ V_{1y} \\ \Omega_{1z} \\ \vdots \\ V_{Nx} \\ V_{Ny} \\ \Omega_{Nz} \end{pmatrix} = \boldsymbol{\mu} \cdot \begin{pmatrix} F_{1x} \\ F_{1y} \\ T_{1z} \\ \vdots \\ F_{Nx} \\ F_{Ny} \\ T_{Nz} \end{pmatrix}$$

$\mu$ : N-sphere quasi-2D mobility

- Construct $\mu$ in form of multiple scattering series
- Use symmetry-adjusted multipole functions for spheres + images

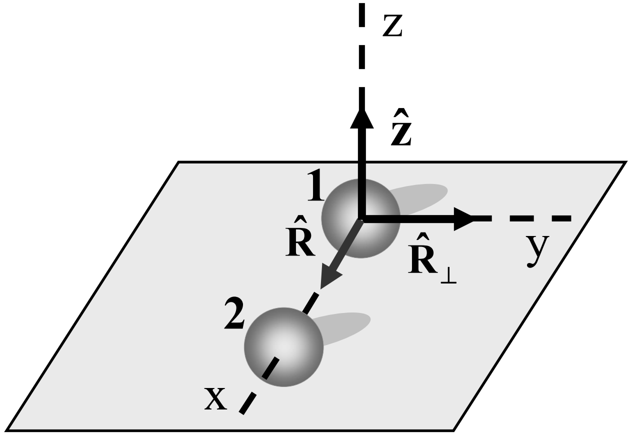
→ numerical results for N > 2 spheres using truncated multipole expansions

→ analytic results for widely separated spheres

- Form of quasi-2D mobilities for two spheres :

$$\begin{pmatrix} V_{1L} \\ V_{1T} \end{pmatrix} = \boldsymbol{\mu}_{11}^{tt} \begin{pmatrix} F_{1L} \\ F_{1T} \end{pmatrix} + \boldsymbol{\mu}_{12}^{tt} \begin{pmatrix} F_{2L} \\ F_{2T} \end{pmatrix} + \boldsymbol{\mu}_{11}^{tr} T_{1z} + \boldsymbol{\mu}_{12}^{tr} T_{2z}$$

$$\Omega_{1z} = \boldsymbol{\mu}_{11}^{rt} \begin{pmatrix} F_{1L} \\ F_{1T} \end{pmatrix} + \boldsymbol{\mu}_{12}^{rt} \begin{pmatrix} F_{2L} \\ F_{2T} \end{pmatrix} + \mu_{11}^{rr} T_{1z} + \mu_{12}^{rr} T_{2z}$$



self mobilities: 1-1

distinct mobilities: 1-2

Longitudinal (x - x): $\parallel \ \hat{\mathbf{R}} = (\mathbf{r}_2 - \mathbf{r}_1)/r$

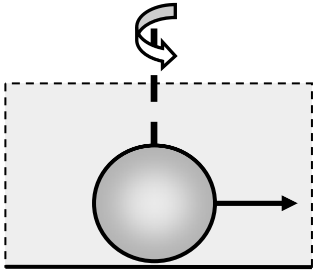
Transversal (y - y): $\parallel \ \hat{\mathbf{R}}_\perp = \hat{\mathbf{z}} \times \hat{\mathbf{R}}$

- Self-mobilities for R = r/(2a) >> 1

$$\mu_{11}^{tt} = \frac{1}{6\pi\eta_0 a}\begin{pmatrix} 1.3799544\ldots & 0 \\ 0 & 1.3799544\ldots \end{pmatrix} + o(1/R^3)$$

$$\mu_{11}^{rr} = \frac{1.10920983\ldots}{8\pi\eta_0 a^3} + o(1/R^3)$$

$$D_0^{r,2D} \approx 1.11\, D_0^{r,3D}$$



$$D_0^{t,2D} \approx 1.38\, D_0^{t,3D}$$

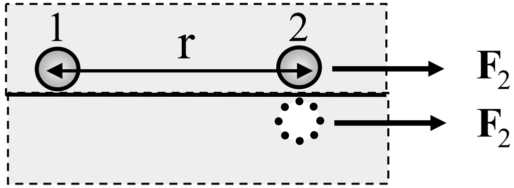
- Distinct mobilities for R >> 1

Q-2D :

$$\mu_{12}^{tt} = \frac{1}{6\pi\eta_0 a}\left[\frac{1}{R}\begin{pmatrix} 3/2 & 0 \\ 0 & 3/4 \end{pmatrix} - \frac{1}{R^3}\begin{pmatrix} 1.159862\ldots & 0 \\ 0 & 0.111686\ldots \end{pmatrix}\right] + o(1/R^3)$$

3D :

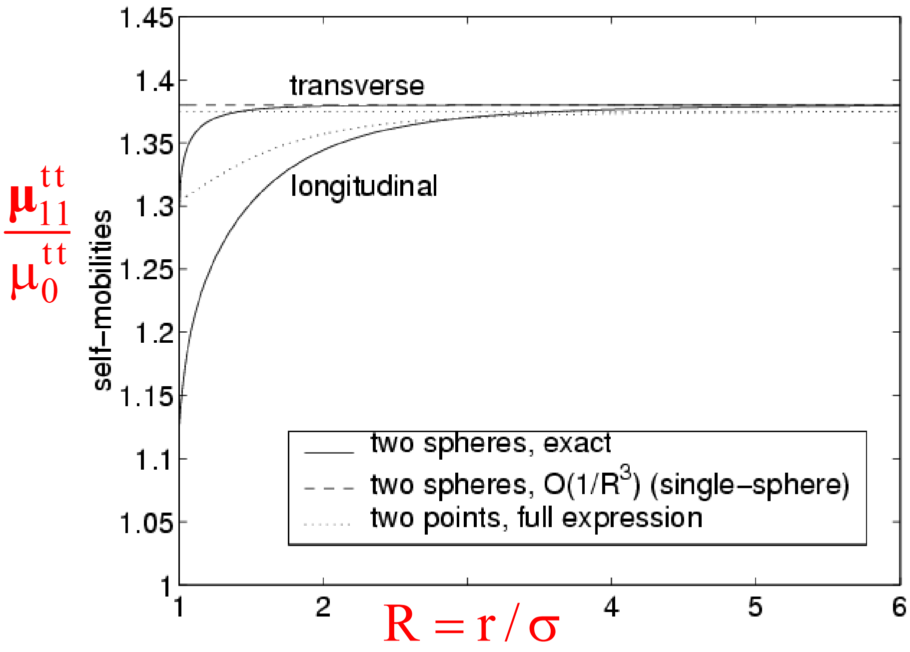
$$\left(\mu_{12}^{tt}\right)_{RP}^{3D} = \frac{1}{6\pi\eta_0 a}\left[\frac{1}{R}\begin{pmatrix} 3/4 & 0 \\ 0 & 3/8 \end{pmatrix} - \frac{1}{R^3}\begin{pmatrix} 1/8 & 0 \\ 0 & -1/16 \end{pmatrix}\right]$$

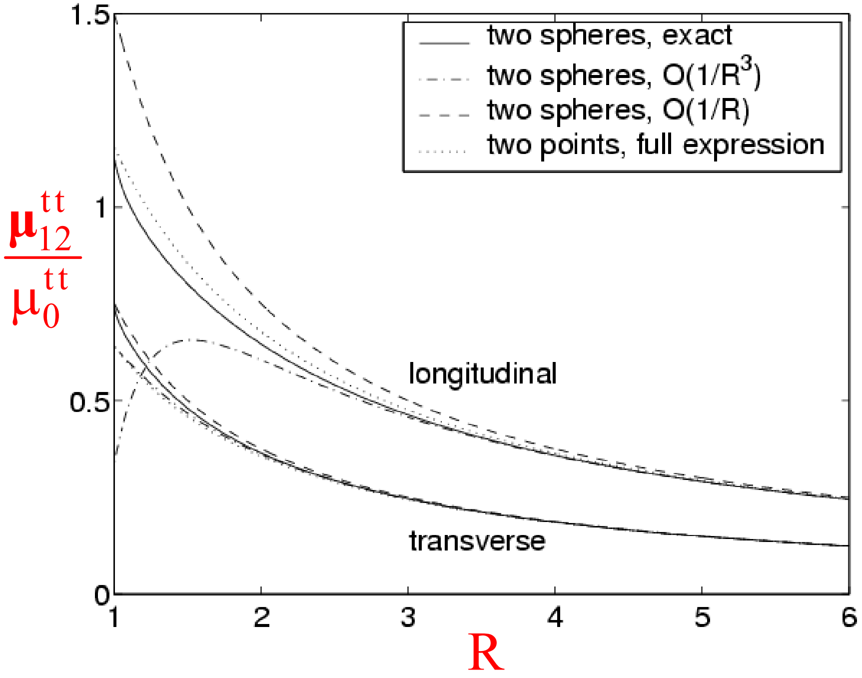


$$\mu_{12}^{tr} = \frac{\mu_0^{rt}}{4R^2}\begin{pmatrix} 0 \\ -1 \end{pmatrix} + o(1/R^3) \quad , \quad \mu_{12}^{rr} = -\frac{\mu_0^{rr}}{8R^3} + o(1/R^3) \quad , \quad \mu_0^{rt} = \left(4\pi\eta_0 a^2\right)^{-1}$$

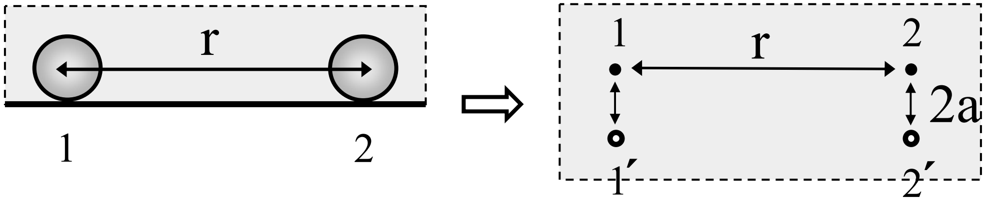
$$\mu_{11}^{tr} = o(1/R^3) \quad ,$$

# Accuracy of long-distance approximations for 2-sphere mobilities





- Include also results from point-particle model (PPM)

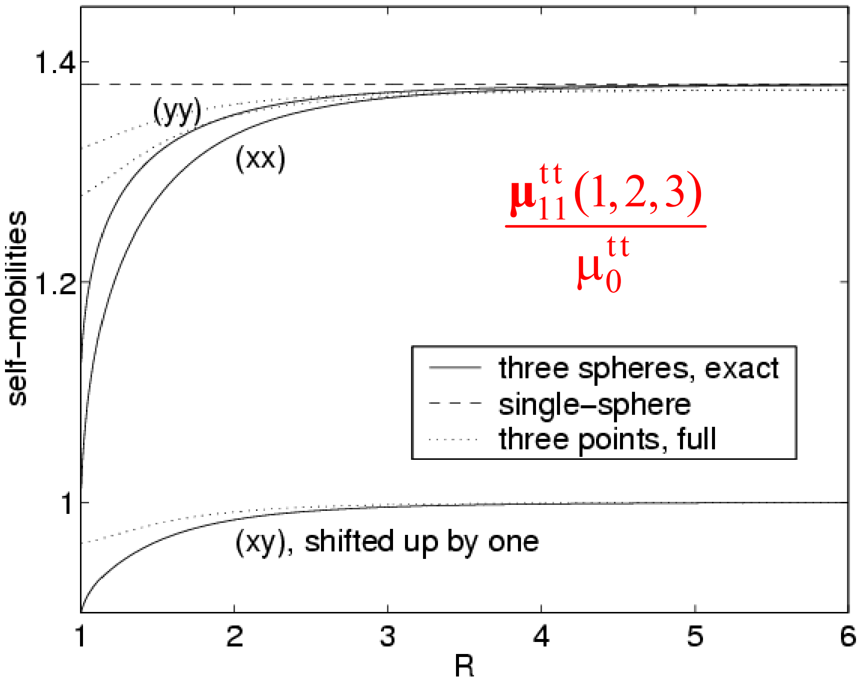


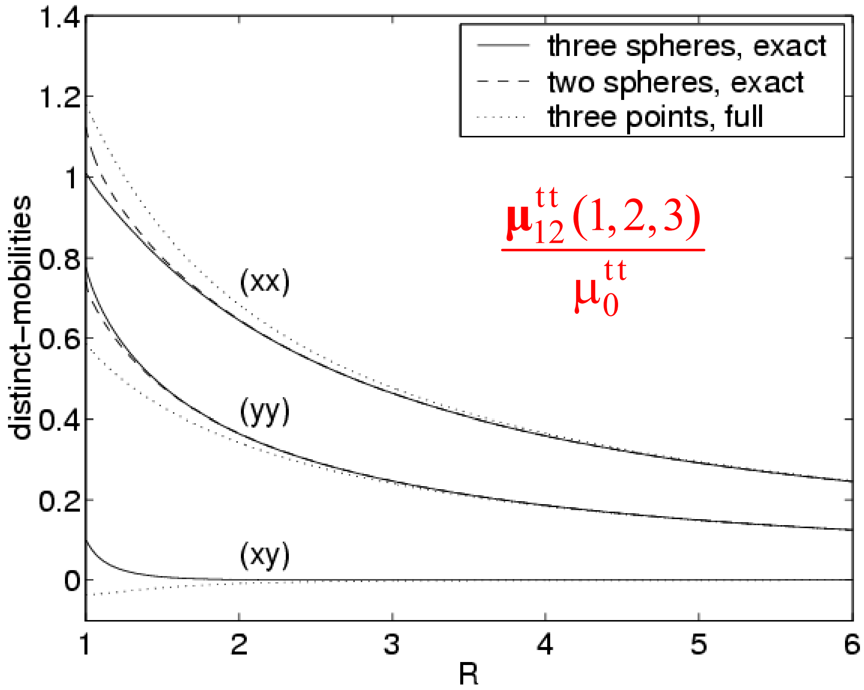
$\mathrm{dist}(p - p') = 2a = \sigma$

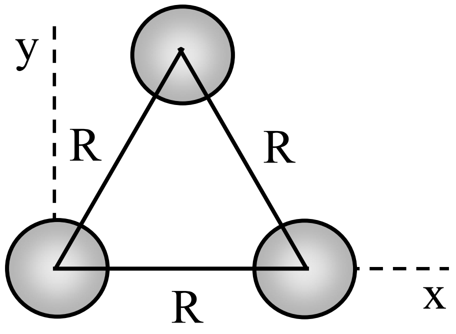
- PPM not pairwise additive for N > 2 due to vertical constraint forces

( Cichocki, Ekiel-Jezewska, G.N., Waijnryb, JCP 121 & Europhys. Lett. 67 (2004) )

# 3-body mobilities for equilateral triangle







- $o(R^{-3})$ asymptotic form works well for $R = r/(2a) \geq 2.5$

Particles at free planar interface :

→ quasi-2D mobilities salient input to simulation and theory

→ experimental test of rotational constraints ?

# 6. Basic properties of Smoluchowski dynamics

- Fundamental solution and time correlation functions
- Backward operator and eigenfunction expansion
- Brownian dynamics simulations
- Projection operators and memory equations

# Fundamental solution and time correlation functions

$$\frac{\partial}{\partial t} P(\mathbf{r}^N,t) = \hat{O}(\mathbf{r}^N)P(\mathbf{r}^N,t)$$

$$\int d\mathbf{r}^N \, P(\mathbf{r}^N,t) = 1$$

$$\hat{O}(\mathbf{r}^N) = \sum_{i,j=1}^{N} \nabla_i \cdot \mathbf{D}_{ij} \cdot \left[ \nabla_j - \beta\left(\mathbf{F}_j^p + \mathbf{F}_j^{ex}\right)\right]$$

$$= \nabla \cdot \mathbf{D}(X) \cdot \left[\nabla - \beta \mathbf{F}^T(X)\right]$$

real operator

- Conditional Pdf  $P(\mathbf{r}^N,t \mid \mathbf{r}^N_0,0)$  of finding config. $\mathbf{r}^N$ at t given system was earlier in $\mathbf{r}^N_0$ at t=0 :

$$P(\mathbf{r}^N, t=0 \mid \mathbf{r}_0^N, 0) = \delta(\mathbf{r}^N - \mathbf{r}_0^N)$$

system is with probability 1 in config. $\mathbf{r}^N_0$ at t = 0

$$P(\mathbf{r}^N, t \mid \mathbf{r}_0^N, 0) = e^{\hat{O}(\mathbf{r}^N)t}\,\delta(\mathbf{r}^N - \mathbf{r}_0^N) = \left[\mathbf{1} + t\hat{O} + \frac{t^2}{2}\hat{O}^2 + \ldots\right]\delta(\mathbf{r}^N - \mathbf{r}_0^N)$$

formal solution

$$P(\mathbf{r}^N, t; \mathbf{r}_0^N, 0) = P(\mathbf{r}^N, t|\mathbf{r}_0^N, 0)\,P_{in}(\mathbf{r}_0^N)$$

joint Pdf for system in $\mathbf{r}^N$ at t and $\mathbf{r}^N_0$ at t = 0

---

- Knowledge of conditional & initial Pdf suffice to determine all relevant dynamic properties
- Example : equilibrium MSD for $P_{in}(\mathbf{r}^N) = P_{eq}(\mathbf{r}^N)$

$$\left\langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \right\rangle = \int d\mathbf{r}^N \int d\mathbf{r}_0^N \, P(\mathbf{r}^N, t|\mathbf{r}_0^N, 0) P_{eq}(\mathbf{r}_0^N)[\mathbf{r}_i - \mathbf{r}_{i0}]^2$$

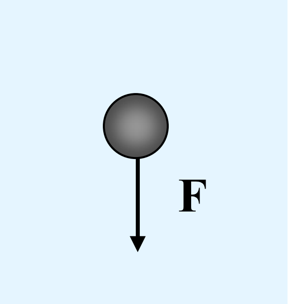
Example: fundamental solution for single particle under constant external force

$$\frac{\partial}{\partial t} P_1(\mathbf{r},t) = D_0 \nabla^2 P_1(\mathbf{r},t) - \beta D_0 \mathbf{F} \cdot \nabla P_1(\mathbf{r},t)$$

(unbound quiescent fluid)

$$P_1(\mathbf{r},t\,|\,\mathrm{r}_0,0) = \left(4\pi D_0 t\right)^{-3/2} \exp\left\{-\frac{(\mathbf{r}-\mathbf{r}_0-\beta D_0 \mathbf{F}\,t)^2}{4 D_0 t}\right\}$$

$$P_1(\mathbf{r},0\,|\,\mathbf{r}_0,0) = \delta(\mathbf{r}-\mathbf{r}_0)$$



$$\left\langle \mathbf{r}(t)-\mathbf{r}(0)\right\rangle = \left(\beta D_0 \mathbf{F}\right) t$$

$$\left\langle \left(\mathbf{r}(t)-\mathbf{r}(0)\right)^2 \right\rangle = 6 D_0\, t + \left(\beta D_0 \mathbf{F}\right)^2 t^2$$

- Uniform diffusion in co-moving system with drift velocity $\beta D_0 \mathbf{F}$

- $P_1^{eq}(\mathbf{r}) = P_1(\mathbf{r}, t \to \infty) = V^{-1}$

- Equilbrium time correlation function of two configurational functions A(X) and B(X) :

$$C_{AB}(t) = \left\langle A^*(\mathbf{r}^N(t))\, B(\mathbf{r}^N(0)) \right\rangle := \int d\mathbf{r}^N \int d\mathbf{r}_0^N\, A^*(\mathbf{r}^N)\, B(\mathbf{r}_0^N)\, P(\mathbf{r}^N, t \,|\, \mathbf{r}_0^N, 0)\, P_{eq}(\mathbf{r}_0^N)$$

- Very often: A is Fourier component of a conserved density variable

$$A = A_{\mathbf{q}} \propto \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} a(\mathbf{r}; X) \qquad a(\mathbf{r}; X) = \sum_{j=1}^{N} a_j\, \delta(\mathbf{r} - \mathbf{r}_j)$$

conserved property

$a_j = 1$ : collective diffusion

$a_j = \delta_{j1}$: self-diffusion of 1

$$A_{\mathbf{q}} = c_{\mathbf{q}} \equiv \frac{1}{\sqrt{N}} \sum_{l=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_l} - \sqrt{N}\, \delta_{\mathbf{q},0}$$

$$A_{\mathbf{q}} = a_{\mathbf{q}} \equiv e^{i\mathbf{q}\cdot\mathbf{r}_1} - \delta_{\mathbf{q},0}$$

$$S(q,t) = \lim_{\infty} \left\langle c_{-\mathbf{q}}(0)\, c_{\mathbf{q}}(t) \right\rangle \qquad G(q,t) = \lim_{\infty} \left\langle a_{-\mathbf{q}}(0)\, a_{\mathbf{q}}(t) \right\rangle$$

Dynamic structure factor

Self-dynamic structure factor

# Backword operator and eigenfunction expansion

- Define two unitary products on space of configuration variables

$$(\mathrm{A}\,|\,\mathrm{B}) := \int d\mathbf{r}^{N} \mathrm{A}^{*}(\mathbf{r}^{N})\mathrm{B}(\mathbf{r}^{N}) \qquad \langle \mathrm{A}\,|\,\mathrm{B}\rangle := \int d\mathbf{r}^{N} \mathrm{P}_{eq}(\mathbf{r}^{N})\,\mathrm{A}^{*}(\mathbf{r}^{N})\,\mathrm{B}(\mathbf{r}^{N}) = \langle \mathrm{A}^{*}\mathrm{B}\rangle_{eq}$$

unweighted product

weighted product

- Define backword Smoluchowski operator as adjoint operator w/r to (..|..) :

$$(\hat{\mathrm{O}}_{\mathrm{B}}\mathrm{A}\,|\,\mathrm{B}) = (\mathrm{A}\,|\,\hat{\mathrm{O}}\,\mathrm{B}) \quad \Rightarrow$$

$$\boxed{\begin{aligned}\hat{\mathrm{O}}_{\mathrm{B}}(\mathbf{r}^{N}) &= \sum_{i,j=1}^{N}\left[\nabla_{i} + \beta\left(\mathbf{F}_{i}^{p} + \mathbf{F}_{i}^{ex}\right)\right]\cdot\mathbf{D}_{ij}\cdot\nabla_{j} \\ &= \left[\nabla + \beta\mathbf{F}^{T}(\mathrm{X})\right]\cdot\mathbf{D}(\mathrm{X})\cdot\nabla\end{aligned}}$$

- Some useful properties of real backward Smoluchowski operator :

(a) $\langle \hat{\mathrm{O}}_{\mathrm{B}}\mathrm{A}\,|\,\mathrm{B}\rangle = \langle \mathrm{A}\,|\,\hat{\mathrm{O}}_{\mathrm{B}}\,\mathrm{B}\rangle$ self-adjoint w/r to weighted inner product

(b) $\hat{\mathrm{O}}\left(\mathrm{A}\,\mathrm{P}_{eq}\right) = \mathrm{P}_{eq}\hat{\mathrm{O}}_{\mathrm{B}}\mathrm{A}$ for arbitrary A(X) taken at **same** X

- More on useful properties of backward Smoluchowski operator

(c) $$\left\langle A \,|\, \hat{O}_B\, B \right\rangle = -\sum_{i,j=1}^{N} \left\langle \left(\nabla_i A^*\right) \cdot \mathbf{D}_{i\,j}(\mathbf{r}^N) \cdot \nabla_j B \right\rangle_{eq}$$ for arbitrary A and B

real and positive definite 3N x 3N matrix

(d) $$\boxed{\left\langle A \,|\, \hat{O}_B\, A \right\rangle \leq 0}$$ negative semi-definite w/r to <..|..>

- Equilibrium time correlation functions are very conveniently expressed as :

(e) $$\boxed{C_{A\,B}(t) = \left\langle A \,|\, e^{\hat{O}_B\, t}\, B \right\rangle = \left\langle A^* \left(e^{\hat{O}_B\, t}\, B\right) \right\rangle_{eq} = \int d\mathbf{r}^N\, P_{eq}(\mathbf{r}^N)\, A^*(\mathbf{r}^N) \left(e^{\hat{O}_B\, t}\, B(\mathbf{r}^N)\right)}$$

acts like
**time-evolution operator**

- This allows formal definition : $A(t) := e^{\hat{O}_B t} A \quad (A = A(0))$

$$\dot{A} = \hat{O}_B\, A$$

- Example: coarse-grained drift velocity of particle i due to DI and HI :

$$\boxed{\mathbf{v}_i^I(\mathbf{r}^N) := \hat{O}_B\, \mathbf{r}_i = \sum_{l=1}^{N} \left(\beta\, \mathbf{D}_{il} \cdot \mathbf{F}_l^T + \nabla_l \cdot \mathbf{D}_{il}\right) \rightarrow \beta\, D_0 \cdot \mathbf{F}_i^T}$$

- Backward op.is also very useful to express conditional or non-equil. averages :

$$\langle(\ldots)\rangle_{\text{neq}}(t)=\int d\mathbf{r}^N\, P(\underset{\uparrow}{\mathbf{r}^N},t)(\ldots) \qquad \langle(\ldots)\rangle_{X_0}(t)=\int d\mathbf{r}^N\, P(\mathbf{r}^N,t\,|\,\mathbf{r}_0^N,0)(\ldots)$$

arbitrary non-eq.
pdf solution of GSE

(e)

$$\left\langle A(\mathbf{r}^N)\right\rangle_{\text{neq}}(t)=\int d\mathbf{r}^N\, P(\mathbf{r}^N,t=0)\,e^{\hat{O}_B t}A(\mathbf{r}^N)$$

$$\left\langle A(\mathbf{r}^N)\right\rangle_{X_0}(t)=e^{\hat{O}_B(\mathbf{r}^N)t}A(\mathbf{r}^N)\Big|_{\mathbf{r}_0^N}$$

---

- Application to position vector of particle i :

$$\langle\mathbf{r}_i\rangle_{X_0}(\Delta t)=e^{\hat{O}_B(\mathbf{r}^N)\Delta t}\,\mathbf{r}_i\Big|_{X_0}=\mathbf{r}_i^0+\hat{O}_B(\mathbf{r}^N)\mathbf{r}_i\Big|_{X_0}\Delta t+O(\Delta t^2)$$

$$\langle\mathbf{r}_i(\Delta t)-\mathbf{r}_i(0)\rangle_{X_0}\equiv\langle\Delta\mathbf{r}_i(\Delta t)\rangle_{X_0}=\mathbf{v}_i^I(\mathbf{r}_0^N)(\Delta t)+O(\Delta t^2)$$

$$\left\langle\Delta\mathbf{r}_i(\Delta t)\,\Delta\mathbf{r}_j(\Delta t)\right\rangle_{X_0}=2\mathbf{D}_{ij}(X_0)\Delta t+O(\Delta t^2)$$

⇨ Brownian Dynamics Simulations

- How is $v^I(X)$ related with velocity appearing in continuity eq. form of GSE ?

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

$$\mathbf{v}_i(X,t) = -\beta \sum_{l=1}^{N} \mathbf{D}_{il} \cdot \left[ \mathbf{F}_l^H = -\mathbf{F}_l^T - \mathbf{F}_l^B \right] = \sum_{l=1}^{N} \mathbf{D}_{il} \cdot \left[ \beta\, \mathbf{F}_l^T - \nabla_l \ln P(X,t) \right]$$

$$\Downarrow$$

$$\left\langle \mathbf{v}_i(X,t) \right\rangle_{neq}(t) = \int dX\ P(X,t)\ \mathbf{v}_i(X,t) = \left\langle \mathbf{v}_i^I(X) \right\rangle_{neq}(t)$$

# Calculation of backward operator:

$\mathbf{D}(X) = \mathbf{D}^T(X)$ is a real 3N x 3N matrix

$$(A\,|\,\hat{O}B) := \int dX\, A^* \nabla \cdot \mathbf{D}(X) \cdot \left[\nabla - \beta \mathbf{F}^T(X)\right] B = -\int dX \left(\nabla A^*\right) \cdot \mathbf{D}(X) \cdot \left[\nabla - \beta \mathbf{F}^T(X)\right] B$$

partial integration

$$= \int dX \left[ B \beta \mathbf{F}^T(X) \cdot \mathbf{D}(X) \cdot \nabla A^* \right] - \int dX \underbrace{\left(\nabla A^*\right) \cdot \mathbf{D}(X) \cdot \nabla B}_{\left(\nabla B\right) \cdot \mathbf{D}(X) \cdot \nabla A^*}$$

partial integration

$$= \int dX\, B \left[\nabla + \beta \mathbf{F}^T(X)\right] \cdot \mathbf{D}(X) \cdot \nabla A^* = \int dX\, B \Big( \underbrace{\left[\nabla + \beta \mathbf{F}^T(X)\right] \cdot \mathbf{D}(X) \cdot \nabla}_{\hat{O}_B(X)} A \Big)^*$$

$$= (\hat{O}_B A\,|\,B)$$

- surface integrals are assumed zero by appropriate outer BCs ($U^{ex}$ may include wall potential)

# Eigenfunction expansion

- $\hat{O}_B$ is real, self-adjoint and negative-semidefinite w/r to $\langle \ldots | \ldots \rangle \;\Rightarrow$
- Assuming completeness, $\hat{O}_B$ has ONB of real eigenfunctions $\{\phi_\lambda (X)\}$ , with eigenvalues $\{-\lambda\} \le 0$

$$\hat{O}_B\,\phi_\lambda = -\lambda\,\phi_\lambda \qquad \hat{O}_B\,(\phi_0 \equiv 1) = 0 \cdot \phi_0 \qquad \langle \phi_\lambda \,|\, \phi_\mu \rangle = \delta_{\mu\lambda} \qquad \sum_\lambda\!\!\!\!\!\int |\phi_\lambda\rangle\langle\phi_\lambda| = \mathbf{1}$$

$$e^{O_B\,t} = e^{O_B\,t}\,\mathbf{1} = \sum_{\lambda\ge 0}\!\!\!\!\!\!\int e^{-\lambda\,t}\,|\phi_\lambda\rangle\langle\phi_\lambda| = |\phi_0\rangle\langle\phi_0| + \sum_{\lambda>0}\!\!\!\!\!\!\int e^{-\lambda\,t}\,|\phi_\lambda\rangle\langle\phi_\lambda|$$

Spectral representation

$$P(X,t\,|\,X_0,0) = e^{\hat{O}(X)\,t}\,\delta(X - X_0) = e^{\hat{O}_B(X_0)\,t}\,\delta(X - X_0) = P_{eq}(X)\left[1 + \sum_{\lambda>0}\!\!\!\!\!\!\int e^{-\lambda\,t}\,\phi_\lambda(X_0)\,\phi_\lambda(X)\right]$$

$$P(X,t\,|\,X_0,0) \;\rightarrow\; P_{eq}(X) \quad \text{for } t \;\rightarrow\; \infty$$

Conditional Pdf evolves monotonically towards equilibrium Pdf

$$P(X,t\,|\,X_0,0)\,P_{eq}(X_0) = P(X_0,t\,|\,X,0)\,P_{eq}(X)$$

Detailed balance relation (t > 0)

- Integration of detailed balance relation w/r to X shows that $\hat{O}\,P_{eq} = 0$

- Consequences for equilibrium time correlation functions in Smoluchowski dynamics :

$$C_{AB}(t) = \left\langle A \,|\, e^{\hat{O}_B t}\, B \right\rangle = \sum_{\lambda \geq 0} \int e^{-\lambda t} d\lambda \langle A \,|\, \phi_\lambda \rangle \langle \phi_\lambda \; B \rangle \underbrace{\rightarrow}_{t \rightarrow \infty} \langle A \rangle_{eq} \langle B \rangle_{eq}$$

A and B uncorrelated at long times (fluid)

- Regular autocorrelation functions $C_{AA}(t) \equiv C_A(t)$ are strictly monotonically decaying :

$$\boxed{C_A(t) = \sum_{\lambda \geq 0} \int e^{-\lambda t} \underbrace{\left| \langle A \,|\, \phi_\lambda \rangle \right|^2}_{} \geq 0}$$

$$\boxed{(-1)^n \frac{\partial^n}{\partial t^n} C_A(t) = \sum_{\lambda \geq 0} \int \lambda^n e^{-\lambda t} \left| \langle A \,|\, \phi_\lambda \rangle \right|^2 \geq 0}$$

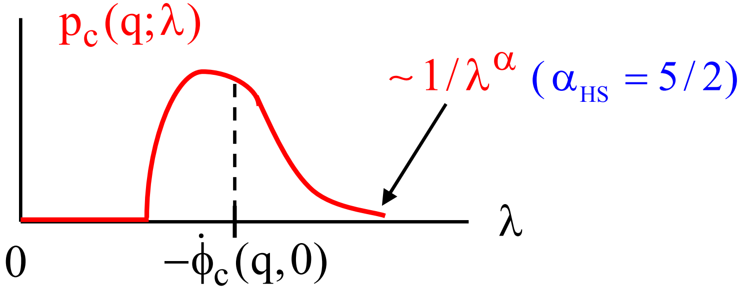
$0 \leq p_A(\lambda)$ : spectral density of $C_A(t)$

- Largest eigenvalue of Smoluchowski operator is non-degenerate,

since all eigenfunctions to $\lambda = 0$ must not change sign for all X

- Example: normalized dynamic structure factor with $A = c_{\mathbf{q}}$ and $\langle A \rangle_{eq} = 0$

$$0 \leq \phi_c(q,t) \equiv \frac{S(q,t)}{S(q)} = \int_0^\infty d\lambda\ e^{-\lambda t}\, p_c(q;\lambda) \leq 1$$



$$\phi_c(q, t \to \infty) \equiv \begin{cases} 0 & \text{fluid} \\ f_c(q) > 0 & \text{„glass“} \end{cases}$$

- Consider Laplace transform of $\phi_c$ (q,t) :

$$\tilde{\phi}_c(q,z) \equiv \int_0^\infty dt\ e^{-zt}\, \phi_c(q,t) \sim \frac{f_c(q)}{z}$$

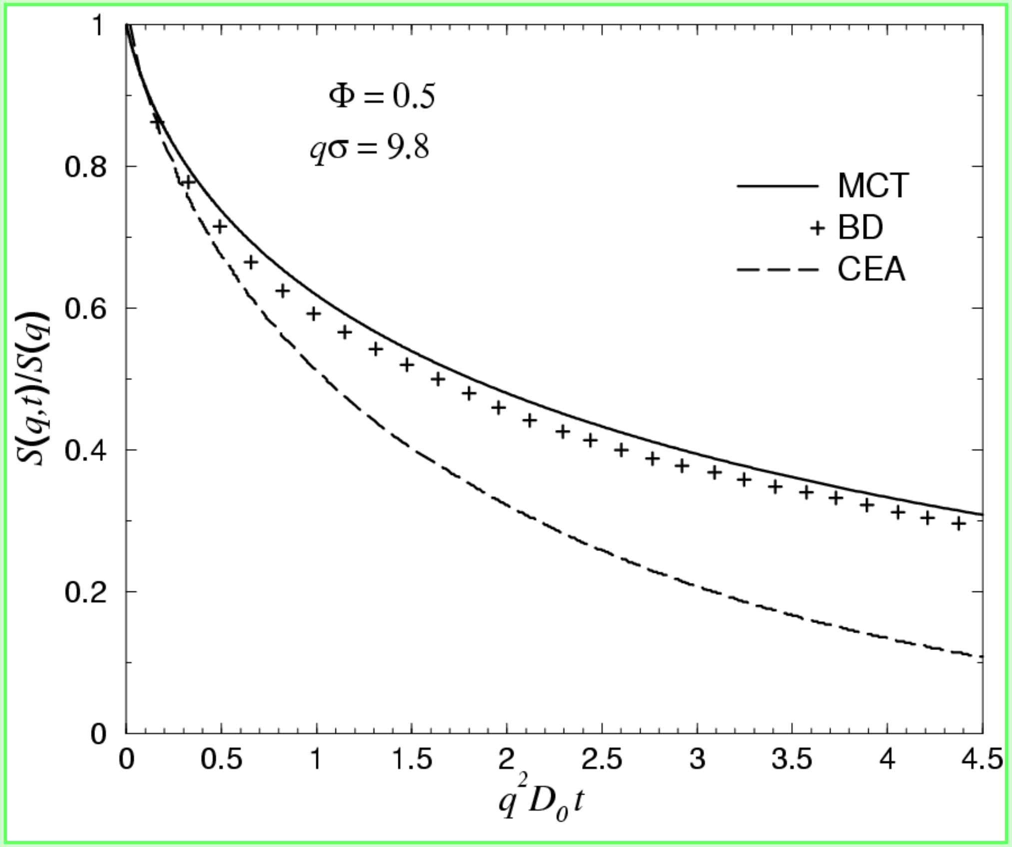
+ regular part

develops 1/z pole at glass point

$$\tilde{\phi}_c(q,z) \equiv \int_0^\infty d\lambda\ e^{-\lambda t}\, \frac{p_c(q,\lambda)}{z+\lambda}$$

singularities only on negative axis in complex z-plane:

# Example: Dynamic structure factor of 3D hard-sphere dispersion



(Banchio, Nägele & Bergenholtz, J. Chem. Phys. 113 (2000))

- S(q,t) decays strictly monotonically in t

# Brownian dynamics simulations

- GSE : $\Delta r^N(\Delta t) = r^N(\Delta t) - r^N(0)$ multivariate Gaussian random process to first order in $\Delta t$ :

$$\left\langle \Delta \mathbf{r}_i(\Delta t) \right\rangle_{X_0} = \mathbf{v}_i^I(\mathbf{r}_0^N)\Delta t + O(\Delta t^2)$$

$$(\tau_B \ll \Delta t \ll \tau_I)$$

$$\left\langle \Delta \mathbf{r}_i(\Delta t)\,\Delta \mathbf{r}_j(\Delta t) \right\rangle_{X_0} = 2\mathbf{D}_{ij}^{tt}(X_0)\Delta t + O(\Delta t^2)$$

- Stochastic finite difference equation for translational motion of torque-free spheres :

$$\Delta \mathbf{r}_i(\Delta t) = \sum_{l=1}^{N}\Big(\beta\,\mathbf{D}_{il}^{tt}(X_0)\cdot \mathbf{F}_l^T(X_0) + \nabla_l \cdot \mathbf{D}_{il}^{tt}(X_0)\Big)\ \Delta t\ +\ \Delta \mathbf{x}_i(\Delta t)$$

DI

Near-field HI

Central Gaussian displacement

$$\left\langle \Delta \mathbf{x}_i(\Delta t)\,\Delta \mathbf{x}_j(\Delta t) \right\rangle = 2\mathbf{D}_{ij}^{tt}(X_0)\,\Delta t$$

$$\left\langle \Delta \mathbf{x}_i(\Delta t) \right\rangle = 0$$

Point particles w/o DI (obey Oseen-HI):

$$\Delta \mathbf{r}_i(\Delta t) = \Delta \mathbf{x}_i(\Delta t)$$

Gaussian now

- For $\mathbf{D} = \mathbf{D}(X)$, care needed for limit $\Delta t \rightarrow 0$ (Ito vs. Stratonovich)

# Stokesian dynamics of non-Brownian spheres

$$\Delta \mathbf{r}_i(\Delta t) = \beta \sum_{l=1}^{N} \mathbf{D}_{il}^{tt}(X_0) \cdot \mathbf{F}_l^{T}(X_0)\ \Delta t + O((\Delta t)^2)$$

$$\mathbf{v}_i = \beta \sum_{l=1}^{N} \mathbf{D}_{il}(\mathbf{r}^N) \cdot \left[\ \mathbf{F}_l^{p} + \mathbf{F}_l^{ex}\ \right] \qquad \frac{\partial}{\partial t} P(\mathbf{r}^N, t) + \sum_{i=1}^{N} \nabla_i \cdot \left( \mathbf{v}_i(\mathbf{r}^N)\ P(\mathbf{r}^N, t) \right) = 0$$

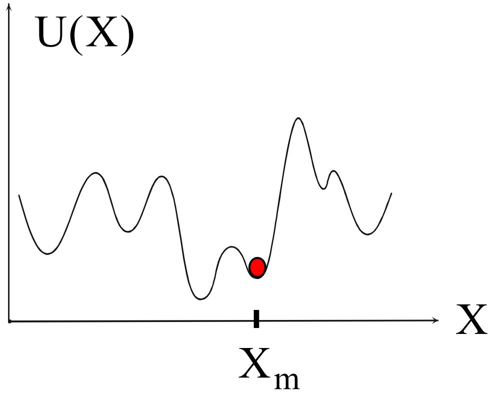
- First-order Stokes-Liouville equation of overdamped motion

$$\frac{\partial}{\partial t} P(\mathbf{r}^N, t) = \hat{O}_{SL}(\mathbf{r}^N) P(\mathbf{r}^N, t) \qquad \hat{O}_{SL}(\mathbf{r}^N) = -\beta \sum_{i,j=1}^{N} \nabla_i \cdot \mathbf{D}_{ij} \cdot \left[ \left( \mathbf{F}_j^{p} + \mathbf{F}_j^{ex} \right) \right]$$

Particles come to rest **without** external forcing at a configuration $X_m$ where U(X) has a local minimum

$$P(X, t \rightarrow "\infty") = \delta(X - X_m)$$

**may depend on start configuration**



P(X,t) = const stationary solution for constant external forcing (sedimentation) only when $\nabla \cdot \mathbf{D}(X) = 0$ (i.e., for point particles only)

# Example: Stokesian dynamics simulation of Q2D system

$$\boxed{\Delta \mathbf{r} = \mathbf{R}_{FU}^{-1}(\mathbf{r}^{N})\cdot \mathbf{F}^{pot}\,\Delta t + k_B T \nabla \cdot \mathbf{R}_{FU}^{-1}(\mathbf{r}^{N})\,\Delta t + \Delta \mathbf{X}}$$

translational-rotational N-sphere displacement

DI

near-field HI

Gaußian random step

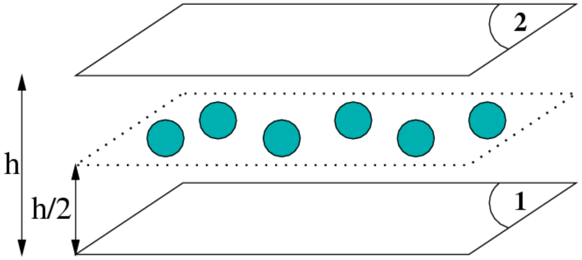
$$\left\langle \Delta \mathbf{X}\, \Delta \mathbf{X} \right\rangle = 2 k_B T\, \mathbf{R}_{FU}^{-1}\, \Delta t$$

mobility matrix (5N × 5N)

$$\mathbf{F}^{hyd} = -\mathbf{R}_{FU}(\mathbf{r}^{N}) \cdot \mathbf{U}$$

HI: multipole expansion + lubrication

- Only mid-plane diffusion considered
- Superposition of single-wall geometry (stick BC)

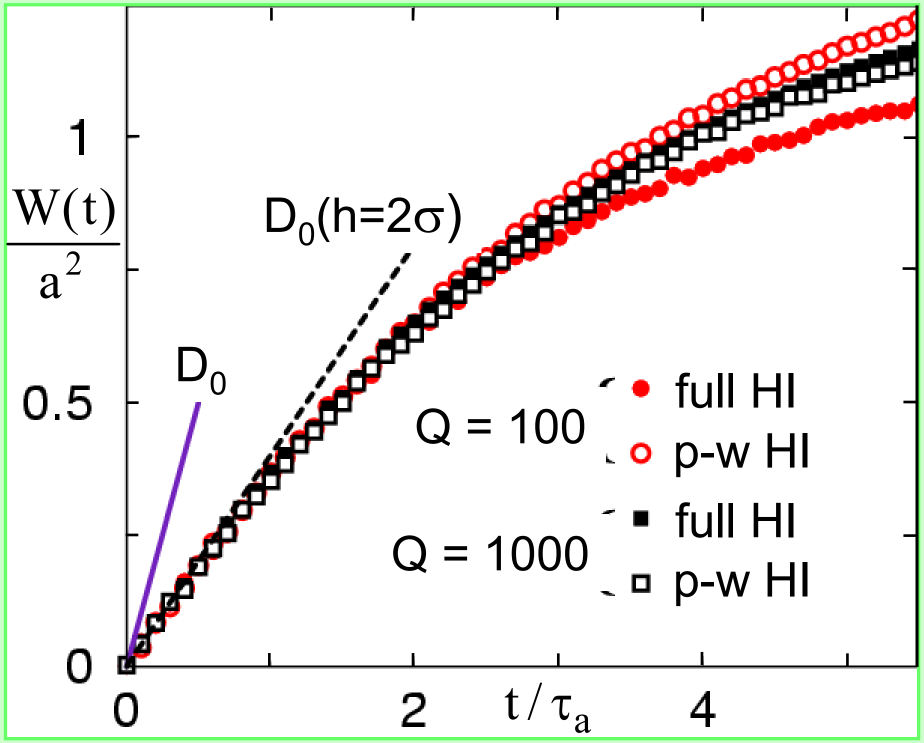


$$\mathbf{F}_i^{hyd} = -\sum_{j=1}^{N} \left\{ \underbrace{\left(\mathbf{R}_{ij}^{pp}\right)_{FU}^{(1)}}_{\text{particle-particle HI \& first wall alone}} + \left(\mathbf{R}_{ij}^{pp}\right)_{FU}^{(2)} + \left[ \underbrace{\left(\mathbf{R}_{ij}^{pw}\right)_{FU}^{(1)}}_{\text{particle-wall HI \& first wall alone}} + \left(\mathbf{R}_{ij}^{pw}\right)_{FU}^{(2)} \right] \delta_{ij} \right\} \cdot \mathbf{U}_j$$

Bossis et al., Phys. Fluids A3 (1991)

# Self-diffusion using Chang-Hone screened Coulomb potential

**Task**: assess individual relevance of p-w and p-p HI for dynamics



$$W(t) = \frac{\left\langle \left[\mathbf{r}(t) - \mathbf{r}(0)\right]^2 \right\rangle}{4}$$

$$\tau_a = a^2 / D_0$$

$$C = 0.063$$

$$h = 2\sigma$$

$$\boxed{D_0(h) \approx 0.4 D_0}$$

$$\kappa^{-1}(h) \approx 0.9\sigma$$

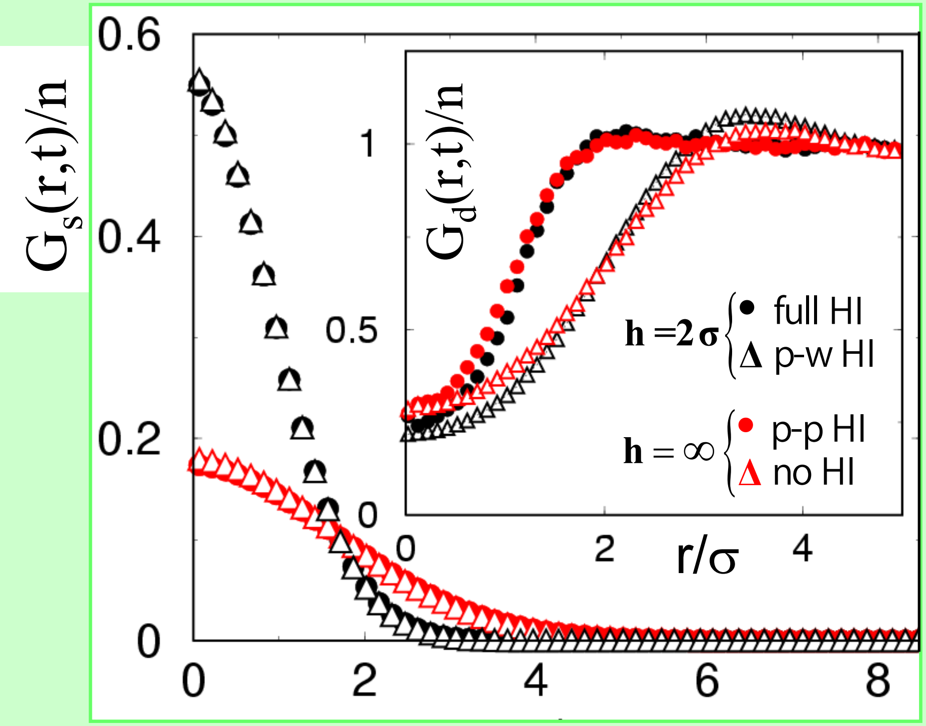
- Small hydrodynamic enhancement by p-p HI for strongly charged spheres
- Self-diffusion lowered for moderately charged or neutral spheres

# Space-time correlations: van Hove functions

Conditional pdf : $$G(r,t)=\left\langle \sum_{i,j=1}^{N}\left[\mathbf{r}-\mathbf{r}_i(t)+\mathbf{r}_j(0)\right]/N\right\rangle = G_s(r,t)+G_d(r,t)$$

Distinct part : $$G_d(r,0)=n\,g(r)\ , \quad n=N/A$$

Self part : $$G_s(r,0)=\delta(\mathbf{r})\ , \qquad G_s(r,t)\approx\frac{1}{4\pi W(t)}\exp\left\{-\frac{r^2}{4W(t)}\right\}$$



$t = 3.5\,\tau_a$

$C = 0.063$

$h = 2\,\sigma$

$Q = 10^3$

SD: Pesché & Nägele
PRE 62 (2000)

- Collective diffusion dominated by p-p HI and self-diffusion by p-w HI

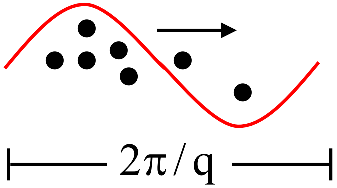
# Projection operators and memory equations

- Evolution of conserved variable A(X) = $A_{\mathbf{q}}$ (X) in Brownian system :

$$A \equiv A_{\mathbf{q}} \propto \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} \sum_{j=1}^{N} a_j\, \delta(\mathbf{r}-\mathbf{r}_j)$$

$$\frac{\partial}{\partial t} A_{\mathbf{q}} \equiv \hat{O}_B A_{\mathbf{q}} = i\mathbf{q}\cdot\mathbf{J}^{A}_{\mathbf{q}} \to 0 \quad , \quad q \to 0$$

slow, at least for q small



$$\hat{P}_A \equiv \frac{|A\rangle\langle A|}{\langle A\,|\,A\rangle}$$

projects on $E_P$
(slow-variable subspace)

$$\hat{Q}_A \equiv \mathbf{1} - \hat{P}_A$$

projects on $E_Q$
(fast-variable subspace)

$$E = E_P \oplus E_Q$$

$$A_{\mathbf{q}} = c_{\mathbf{q}} \equiv \frac{1}{\sqrt{N}} \sum_{l=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_l} - \sqrt{N}\,\delta_{\mathbf{q},0}$$

$$A_{\mathbf{q}} = a_{\mathbf{q}} \equiv e^{i\mathbf{q}\cdot\mathbf{r}_1} - \delta_{\mathbf{q},0}$$

$$S(q,t) = \lim_{\infty} \left\langle c_{\mathbf{q}} \,|\, e^{\hat{O}_B t} c_{\mathbf{q}} \right\rangle$$

dynamic structure factor

$$G(q,t) = \lim_{\infty} \left\langle a_{\mathbf{q}} \,|\, e^{\hat{O}_B t} a_{\mathbf{q}} \right\rangle$$

self-dynamic structure factor

$$\left\langle A_{\mathbf{q}} \right\rangle_{eq} = 0$$

- Memory equation for time evolution of $C_A(t)$ :

$$e^{\hat{O}_B t} = e^{\hat{Q}_A \hat{O}_B t} + \int_0^t du\, e^{\hat{O}_B (t-u)}\, \hat{P}_A \hat{O}_B\, e^{\hat{Q}_A \hat{O}_B u}$$

$$\frac{\partial}{\partial t} C_A(t) = -\omega_A C_A(t) + \int_0^t du\, M_A(t-u)\, \frac{C_A(u)}{C_A(0)}$$

short-time frequency

memory function

$$\omega_A = -\left\langle A \,|\, \hat{O}_B A \right\rangle_A / C_A(0)$$

$$f_A = \hat{Q}_A \hat{O}_B A$$

$$M_A(t) = \left\langle f_A \,|\, e^{\hat{Q}_A \hat{O}_B \hat{Q}_A t} f_A \right\rangle$$

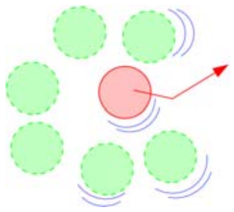
- force – force ACF in fast-variable subspace
- non-negative & strictly monotonically decaying

reduced time evolution operator

$$\frac{C_A(t)}{C_A(0)} = \begin{cases} \exp\{-\omega_A t\} & (\tau_B \ll t \ll \tau_I) \\ \text{slower \& non-exp. in general} & (t \sim \tau_I) \end{cases}$$

- Application: memory equation for dynamic structure factor :

$$\frac{\partial}{\partial t}S(q,t) = \underbrace{-\,q^2 D_0 \frac{H(q)}{S(q)} S(q,t)}_{\tau_B \ll t \ll \tau_I} + \underbrace{\int_0^t du\, M_c(q,t-u)\,\frac{S(q,u)}{S(q)}}_{t \gg \tau_I \ \text{cage relaxation}}$$



$$f_{\mathbf{q}}^c = \hat{O}_B\, c_{\mathbf{q}} + q^2 D_0 \frac{H(q)}{S(q)}\, c_{\mathbf{q}} = i\mathbf{q}\cdot\frac{1}{\sqrt{N}}\sum_{i=1}^{N}\mathbf{v}_i^I + O(q^2)$$

---

- Hydrodynamic function describes short-time dynamics $\tau_B \ll t \ll \tau_I$ :

$$H(q) = \lim_{\infty}\left\langle \frac{1}{N D_0 q^2}\sum_{l,j=1}^{N}\mathbf{q}\cdot\mathbf{D}_{lj}(\mathbf{r}^N)\cdot\mathbf{q}\,\exp[i\mathbf{q}\cdot(\mathbf{r}_l - \mathbf{r}_j)]\right\rangle_{eq} \qquad H(q) \equiv 1 \ \text{w/o HI}$$

$$H(q) = \underbrace{\frac{1}{D_0}\left\langle \hat{\mathbf{q}}\cdot\mathbf{D}_{11}(\mathbf{r}^N)\cdot\hat{\mathbf{q}}\right\rangle_{eq}} + \underbrace{\frac{1}{D_0}\left\langle N\sum_{l\neq j}^{N}\hat{\mathbf{q}}\cdot\mathbf{D}_{12}(\mathbf{r}^N)\cdot\hat{\mathbf{q}}\,\exp[i\mathbf{q}\cdot(\mathbf{r}_1 - \mathbf{r}_2)]\right\rangle_{eq}}$$

$D_S$ : short-time self-diffusion

$H_d(q) \rightarrow 0$ for $q \rightarrow \infty$

# 7.  Short-time dynamics

- Methods of calculation
- Hydrodynamic function
- Sedimentation
- Smoluchowski equation with incident fluid flow
- Collective and gradient diffusion
- Rotational self-diffusion

# Methods of calculation (of short-time properties)

- Brownian/Stokesian dynamics and Lattice-Boltzmann computer simulations

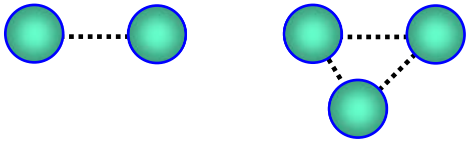
- Leading-order (i.e. zeroth-order) $\delta\gamma$-method (Beenakker & Mazur, 1984, for HS)
    - expansion in renormalized density fluctuations $\delta\gamma$
    - approximate inclusion of many-body HI (ring-diagrams only)
    - truncated 1/r expansion of propagators

    - HS: works rather well for $\phi < 0.35$
    - CS: works well with ext. input for $D_s$ (Banchio & Nägele, 2004)

→ • Truncated hydrodynamic cluster expansion (systems with prevailing far-field HI)

$$\mathbf{D}_{ij}(\mathbf{r}^N) \approx D_0\mathbf{1}\delta_{ij} + \underbrace{\Delta\mathbf{D}_{ij}^{(2)}(\mathbf{r}^N)}_{\text{2-sphere HI}} + \underbrace{\Delta\mathbf{D}_{ij}^{(3)}(\mathbf{r}^N)}_{\text{3-sphere HI}}$$

← static pair- & triplett distribution functions (charged systems)



# Truncated hydrodynamic cluster expansion :

$$\mathbf{D}_{ij}(\mathbf{r}^N) = D_0 \mathbf{1}\delta_{ij} + \underbrace{\Delta\mathbf{D}^{(2)}_{ij}(\mathbf{r}^N)}_{\text{2-body HI}} + \underbrace{\Delta\mathbf{D}^{(3)}_{ij}(\mathbf{r}^N)}_{\text{3-body HI}} + \ldots$$

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

$$\Delta\mathbf{D}^{(2)}_{ij}(\mathbf{r}^N) = D_0\left[\delta_{ij}\sum_{l\neq j}^{N}\boldsymbol{\omega}_{11}(\mathbf{r}_{lj}) + (1-\delta_{ij})\,\boldsymbol{\omega}_{12}(\mathbf{r}_{ij})\right]$$

pairwise-additive

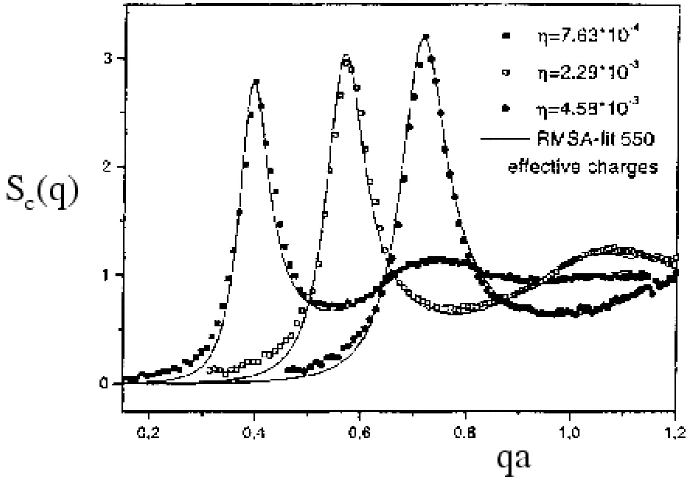
Long-distance multipole expansion of 2-body HI :

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

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

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

# Hydrodynamic function

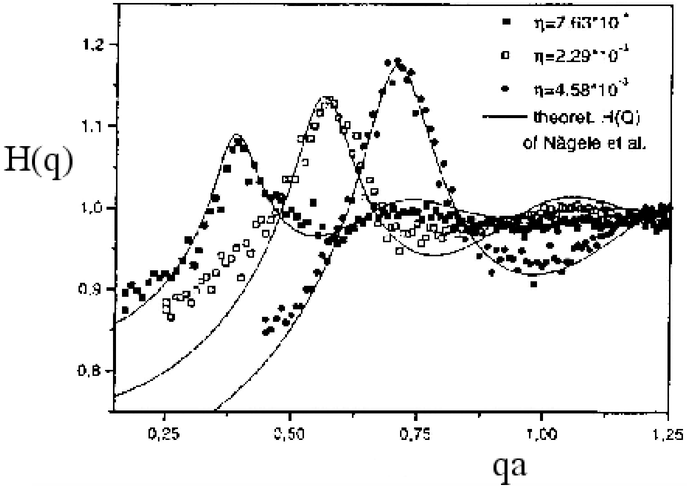


Dilute charge-stabilized dispersions

$\phi \sim 10^{-4}$-$10^{-3}$

(input: RMSA $-$ $g(r)$)

(G. Nägele, general ref. 4 on page 4)

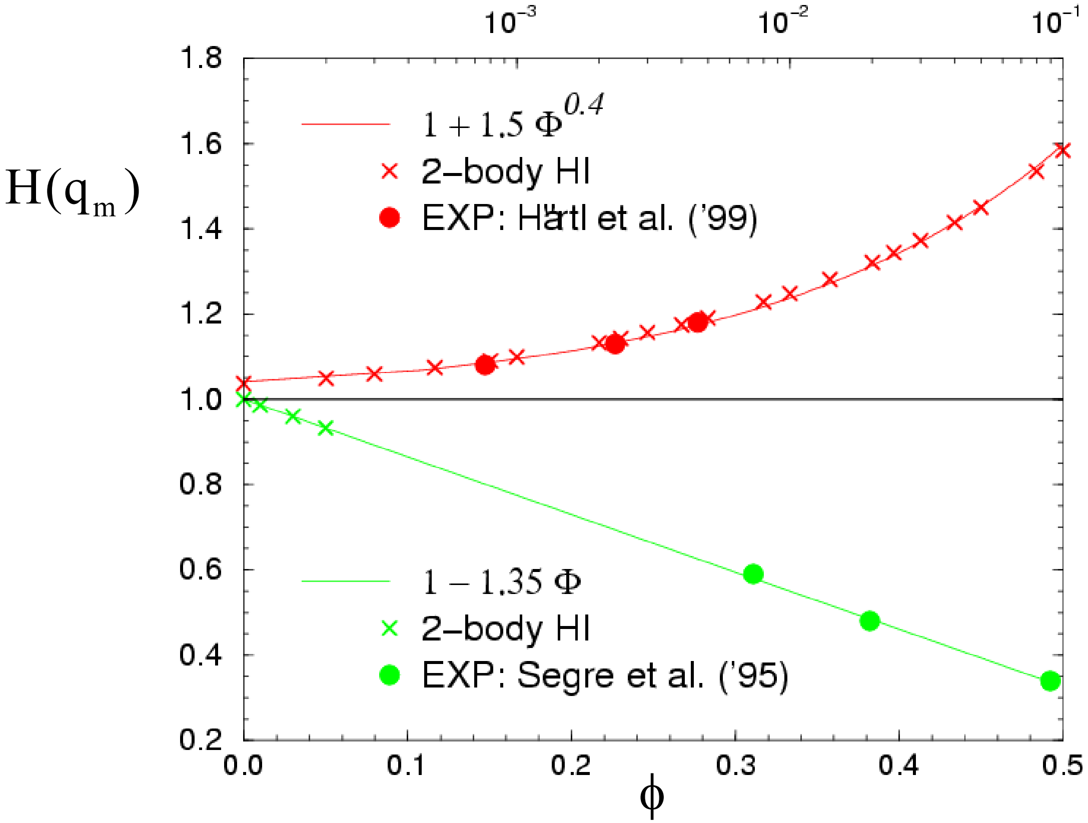


$$H(q_m) \approx 1+1.5\phi^{0.4}$$

$$H(0) \approx 1\text{-}1.8\phi^{1/3}$$

$$H_{RP}(y) = 1 - 15\phi \frac{j_1(y)}{y} + 18\phi \int_1^\infty dx\, x\, h(x) \left( j_0(xy) - \frac{j_1(xy)}{xy} + \frac{j_2(xy}{6x^2} \right), \quad (y = q\sigma)$$

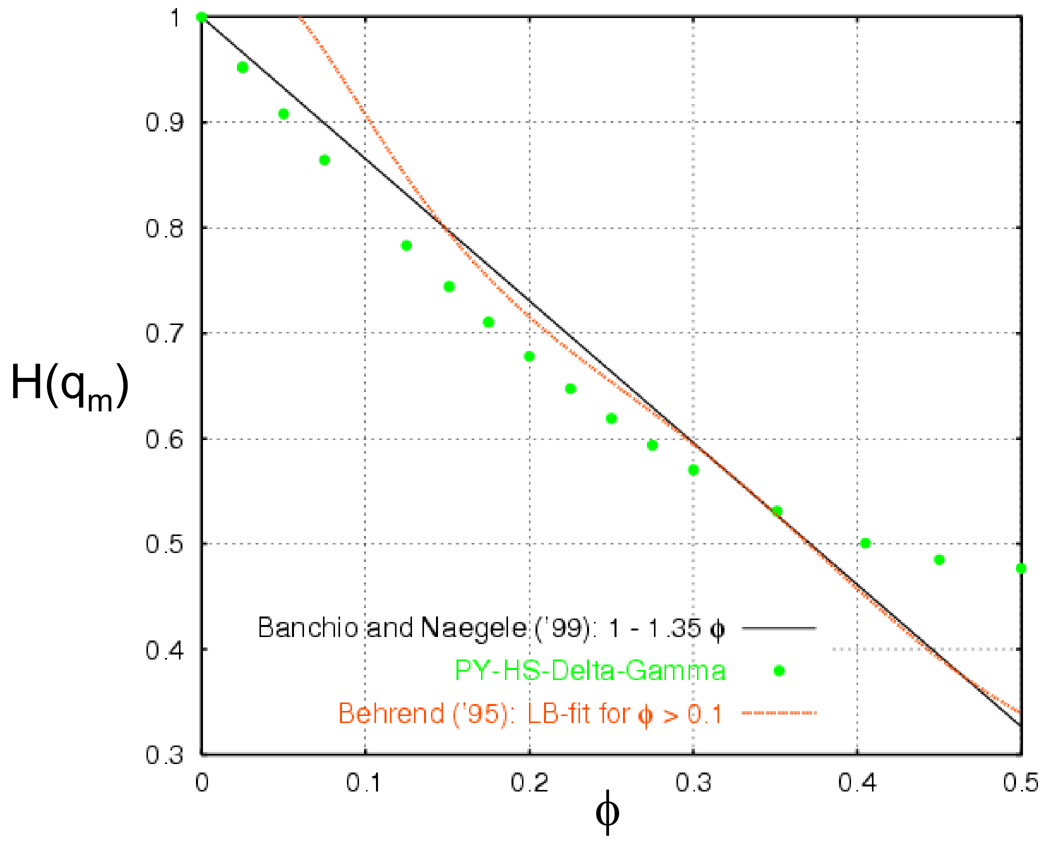
- Peak height $H(q_m)$ vs. concentration



$$H(q_m) \approx \begin{cases} 1 - 1.35\phi & (\mathrm{HS:}\ \phi < 0.5) \\ 1 + p_0\phi^{0.4} & (\mathrm{CS:}\ \phi < 0.05 \text{ and } p_0 = 0.5 - 1.5) \end{cases}$$

(Banchio, Nägele & Bergenholtz, J. Chem. Phys. (1999))

- Peak height $H(q_m)$ for hard spheres



Behrend et al., PRE ´95 :

Lattice-Boltzmann-fit for $\phi > 0.1$

$$\frac{D_0}{D_c(q_m)_{LB}} \approx 1-2\phi+58\phi^2-220\phi^3+347\phi^4$$

combine with:

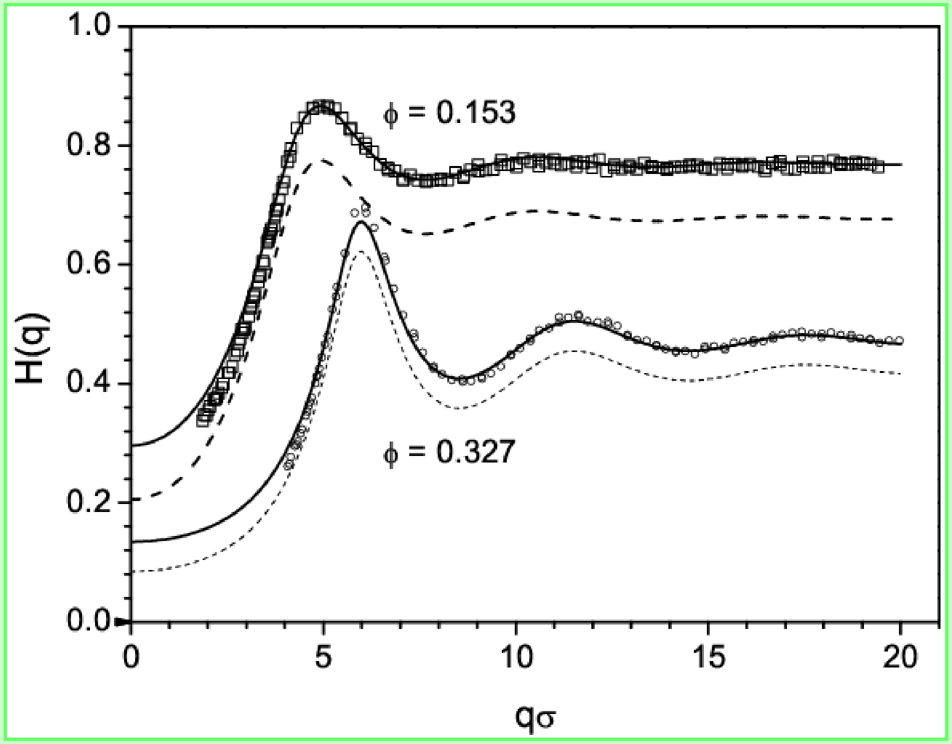
$$S(q_m) = 1 + 0.644\, g_{CS}(\sigma^+;\phi)$$

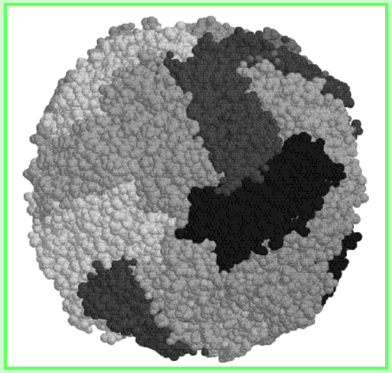
$\Rightarrow$

$$|\,H(q_m)_{LB} - (1-1.35\phi)\,| < 4\%$$

- LB simulations of Ladd in PRE ´95: $H(q_m)$ above $H_{\delta\gamma}(q_m)$ for $\phi$ > 0.4

- H(q) of concentrated charge-stabilized protein dispersions (Apoferritin)





SD simulation vs δγ - calculations

symbols: SD
dashed : δγ
solid: hybrid - δγ

(Gapinski, Banchio, Nägele et al., submitted, 2005)

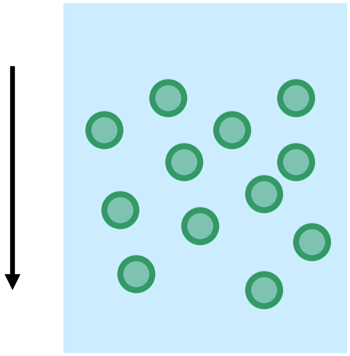
$$H(q) = D_s / D_0 + H_d(q)$$

Input from SD in hybrid - δγ

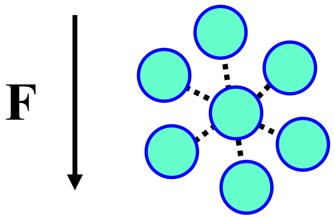
# Sedimentation

- Slow (initial) settling of colloidal Brownian spheres starting from homog. state

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



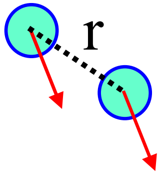
$$U_0 = \beta D_0 F$$



$$\text{Pe} = \frac{\text{diffusion time}}{\text{sedimentation time}} = \frac{\tau_I = \sigma^2 / D_0}{\tau_{sed} = \sigma / U_0} \ll 1$$

$$P_{in}(\mathbf{r}^N, t=0) \underset{t \gg \tau_I}{\underbrace{\rightarrow}} \begin{cases} P_{st}(\mathbf{r}^N) = P_{eq}(\mathbf{r}^N) & \text{no or pairwise-additive HI} \\ P_{st}(\mathbf{r}^N) \neq P_{eq}(\mathbf{r}^N) & \text{3 - and more-body HI} \end{cases}$$

equil. distribution for zero ext. force **F** = 0



**r** fixed for 2-body HI

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

$$0 = \frac{\partial}{\partial t} P_{st}(X) = \sum_{i,j=1}^{N} \nabla_i \cdot \mathbf{D}_{ij} \cdot \left[ \nabla_j - \beta \mathbf{F}_j^p \right] P_{st} - \sum_{i,j=1}^{N} \nabla_i \cdot \mathbf{D}_{ij} \cdot [\beta \mathbf{F} P_{st}]$$

solution : $P_{eq}(X)$

non-eq. drift term

---

$$P_{eq}(X) \propto \exp\{-\beta U\} = \exp\left\{ -\beta \sum_{i<j} u(r_{ij}) \right\}$$ is homogeneous

without HI is : drift term $= \beta D_0 \mathbf{F} \cdot \sum_{i=1}^{N} \nabla_i P_{st} = 0$

$$P_{st}(\mathbf{r}_1 + \mathbf{x}, \ldots, \mathbf{r}_N + \mathbf{x}) = P_{st}(\mathbf{r}_1, \ldots, \mathbf{r}_N) \Rightarrow \sum_i \nabla_i P_{st} = 0$$

with pairwise additive HI is : drift term $= \beta \mathbf{F} \cdot \sum_{i,j=1}^{N} \nabla_i \cdot \mathbf{D}_{ij}^{(2)} P_{eq} = 0$

$$\mathbf{D}_{ij}^{(2)}(\mathbf{r}_1 + \mathbf{x}, \ldots, \mathbf{r}_N + \mathbf{x}) = \mathbf{D}_{ij}^{(2)}(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

- $P_{eq}$ is homog. solution of GSE for pairwise additive HI and DI

- Assume pairwise additive HI :

$$\mathbf{D}_{ij}^{(2)}(\mathbf{r}^N) = D_0 \mathbf{1} \delta_{ij} + \Delta\mathbf{D}_{ij}^{(2)}(\mathbf{r}^N) = D_0 \mathbf{1} \delta_{ij} + D_0 \left[ \delta_{ij} \sum_{l \neq j}^{N} \boldsymbol{\omega}_{11}(\mathbf{r}_{lj}) + (1-\delta_{ij}) \boldsymbol{\omega}_{12}(\mathbf{r}_{lj}) \right]$$

$$\nabla_i \cdot \mathbf{D}_{ij}^{(2)} = \nabla_i \cdot \boldsymbol{\omega}_{12}(\mathbf{r}_i - \mathbf{r}_j) = -\nabla_j \cdot \boldsymbol{\omega}_{12}(\mathbf{r}_i - \mathbf{r}_j) = -\nabla_j \cdot \mathbf{D}_{ij}^{(2)} \quad (i \neq j), \quad \mathbf{D}_{ij}^{(2)} = \mathbf{D}_{ji}^{(2)}$$

---

$$\text{drift term} = \beta \mathbf{F} \cdot \sum_{i,j=1}^{N} \nabla_i \cdot \mathbf{D}_{ij}^{(2)} P_{eq} = \beta P_{eq} \mathbf{F} \cdot \left\{ \sum_{i,j=1}^{N} \nabla_i \cdot \mathbf{D}_{ij}^{(2)} + \beta \sum_{i,j=1}^{N} \mathbf{D}_{ij}^{(2)} \cdot \mathbf{F}_j^p \right\} = 0$$

- Reason for zero drift term :

$$\sum_{i,j=1}^{N} \nabla_i \cdot \mathbf{D}_{ij}^{(2)} = \frac{1}{2} \sum_{i,j=1}^{N}{}' \underbrace{\left( \nabla_i \cdot \mathbf{D}_{ij}^{(2)} + \nabla_j \cdot \mathbf{D}_{ij}^{(2)} \right)}_{=0} + \sum_{i=1}^{N} \nabla_i \cdot \mathbf{D}_{ii}^{(2)}$$

$$\sum_{i=1}^{N} \nabla_i \cdot \mathbf{D}_{ii}^{(2)} = \sum_{i,l=1}^{N}{}' \nabla_i \cdot \omega_{11}(\mathbf{r}_i - \mathbf{r}_l) = \frac{1}{2} \sum_{i,l=1}^{N}{}' \left( \nabla_i \cdot \omega_{11}(\mathbf{r}_i - \mathbf{r}_l) + \nabla_l \cdot \omega_{11}(\mathbf{r}_i - \mathbf{r}_l) \right) = 0$$

$$\beta \sum_{i,j=1}^{N} \mathbf{D}_{ij}^{(2)} \cdot \mathbf{F}_j^p = 0$$ ⇐ zero macroscopic current since pair forces with actio = - reactio

$$\mathbf{F}_j^p = -\sum_{l \neq j} \nabla_j u(r_{jl}) = \sum_{l \neq j} \mathbf{f}_{jl}, \quad (\mathbf{f}_{jl} = -\mathbf{f}_{lj})$$

- Calculation of mean sedimentation velocity $U_{sed}$ at small Peclet numbers :

$$\frac{\partial}{\partial t} P_{st}(X) = 0 = -\sum_{i=1}^{N} \nabla_i \cdot \left( \mathbf{v}_i(X)\; P_{st}(X) \right) \qquad P_{st} = P_{st}(X;\mathbf{F})$$

$$\mathbf{U}_{sed} = \left\langle \frac{1}{N}\sum_{i=1}^{N} \mathbf{v}_i(X) \right\rangle_{st} = \left\langle \frac{1}{N}\sum_{i,l=1}^{N} \beta\, \mathbf{D}_{il} \cdot \left[ \underbrace{\mathbf{F}_l^p - k_B T\, \nabla_l \ln P_{st}(X)}_{\uparrow} + \mathbf{F} \right] \right\rangle_{st} \qquad \mathbf{F}_l^p = -\nabla_l U(X)$$

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

- Since Pe <<1, find from GSE stationary Pdf to linear order in external force :

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

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

$$\mathbf{U}_{sed} = U_{sed}\, \hat{\mathbf{q}}$$

$$\mathbf{v}_i^I = \hat{O}_B^0\, \mathbf{r}_i$$

$$\frac{U_{sed}}{U_0} = \underbrace{\left\langle \frac{1}{N D_0} \sum_{i,l=1}^{N} \hat{\mathbf{q}} \cdot \mathbf{D}_{il} \cdot \hat{\mathbf{q}} \right\rangle_{eq}}_{\uparrow} - \underbrace{\frac{1}{N D_0} \sum_{i,l=1}^{N} \int_0^{\infty} du \left\langle \hat{\mathbf{q}} \cdot \mathbf{v}_i^I\, e^{\hat{O}_B^0 u}\, \hat{\mathbf{q}} \cdot \mathbf{v}_l^I \right\rangle_{eq}}_{\uparrow}$$

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

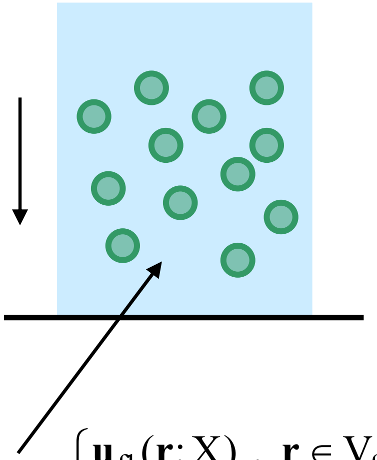
memory-part (zero for PA-HI)
(Green-Kubo-type formula)

# Short-time transport property ≤ Long-time transport property

- Smoluchowski's paradoxon :

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

- Resolution : macroscop. solvent backflow due to container boundaries



$$\mathbf{u}(\mathbf{r};X) = \begin{cases} \mathbf{u}_{fl}(\mathbf{r};X) \ , & \mathbf{r} \in V_{fl} \\ \mathbf{v}_i \ , & \mathbf{r} \in V_i \end{cases}$$

- consider container bottom explicitly (Mazur & van Saarlos, ´78)
- use zero volume flux condition for planes ⊥ to **F** (Batchelor, ´72)

$$\underbrace{\int_{V_c} d\mathbf{r} \left\langle \mathbf{u}(\mathbf{r};X) \right\rangle_{st}}_{V_c \langle \mathbf{u} \rangle_{sa}} = \mathbf{0} = \int dS_\perp \left\langle \mathbf{u}(\mathbf{r};X) \right\rangle_{st}$$

rest frame of container

$$-\nabla \langle p \rangle_{sa} = -\rho\, \mathbf{F}$$

drives backflow

- use that : $\boxed{U_{sed}^{S} - \left\langle \mathbf{u}(\mathbf{r};X) \right\rangle = U_0 \lim_{q\to 0} \lim_{\infty} H(q) \neq U_0\, H(q=0)}$

relative to ensemble averaged volume flow velocity, then
container-shape & position independent (c.f. intrinsic convection)

Assume spatially periodic weak external force is acting on each sphere :

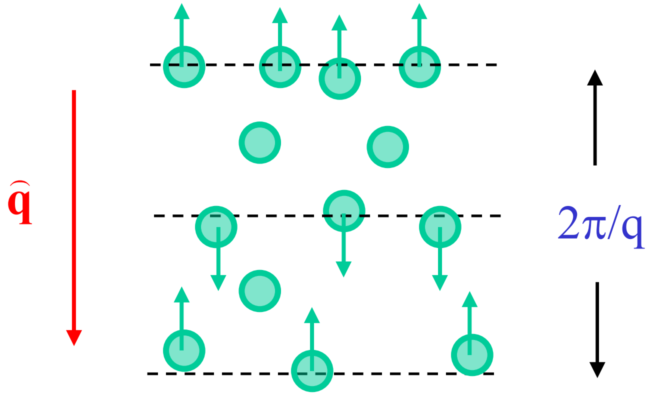
$$\mathbf{F}_j^{ext} = \hat{\mathbf{q}}\, F(q)\, \exp\left[-i\mathbf{q}\cdot\mathbf{r}_j\right]$$

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

$$\boxed{\begin{gathered}\frac{\langle V(q)\rangle}{U_0(q)} = H(q) \\ \lim_{q\to 0}\langle V(q)\rangle = U^S_{sed}\end{gathered}}$$



$$U_0(q) = b_0 F(q) = \beta D_0 F(q)$$

- no macroscopic backflow for non-macroscopic $q^{-1}$ (no regularization necessary)

- $U_{sed}^{L} = U_{sed}^{S} - \Delta U_{sed}^{L}$ : long-time part usually small (needs regularization, too)

hard spheres (HS): $|\Delta U_s^L| \;/\; U_s^S \;<\; 6\ \%$ (at $\phi = 0.45$)

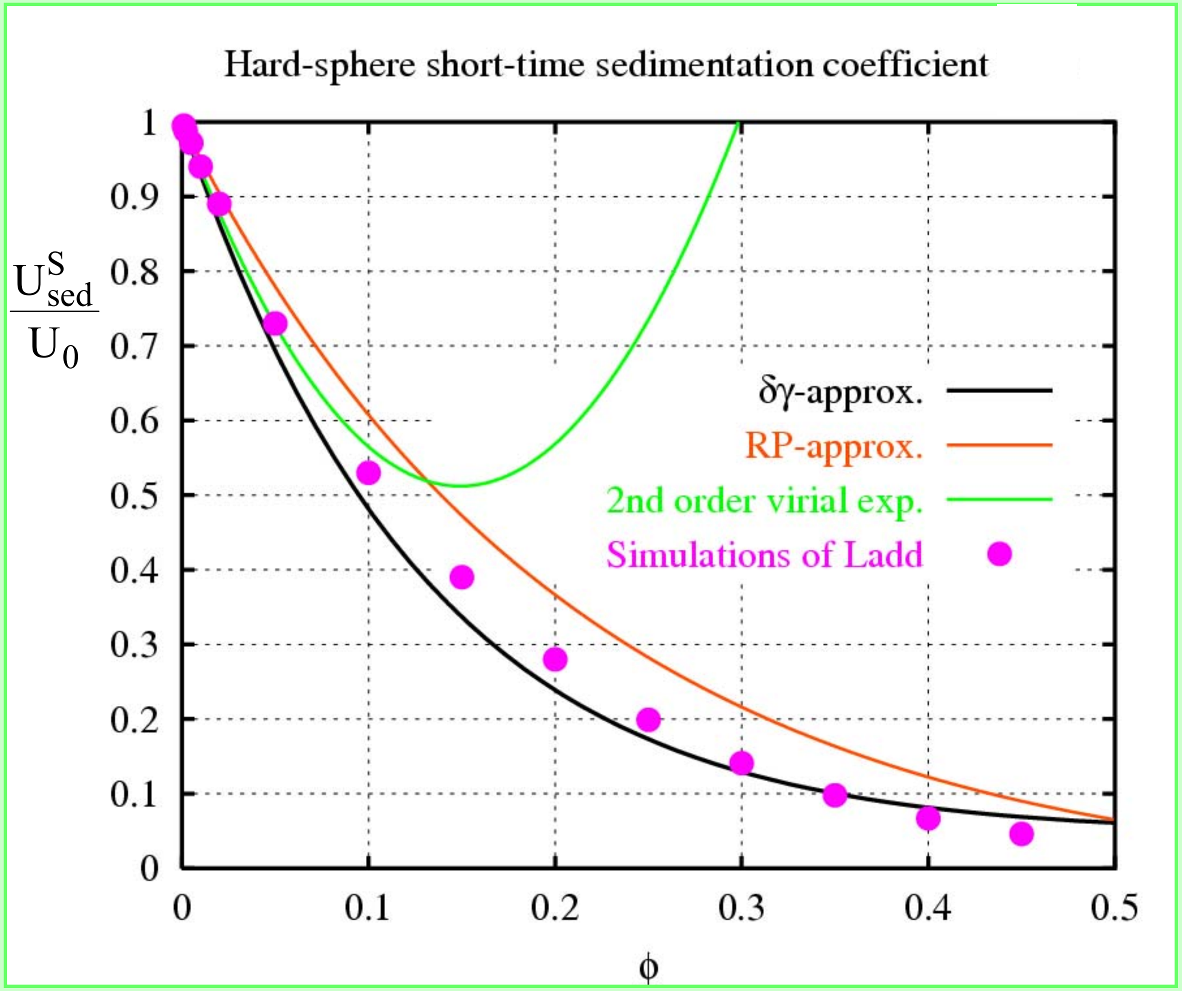
charged spheres (CS): $\begin{cases} \text{comparably small (no lubrication)} \\ \text{truncated 2-body HI sufficient for } \phi < 5-15\ \% \end{cases}$

---

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

$$\frac{U_{sed}^{S}}{U_0} = 1 - \phi \left[ 5 + \underbrace{12\int_1^\infty dx\ x\ (1 - g(x;\phi))}_{\text{known analytically for hard spheres in PY}} + \frac{15}{8}\int_1^\infty dx\ \frac{g(x;\phi)}{x^2} \right] \qquad x = r/2a$$

$$\left(\frac{U_{sed}^{S}}{U_0}\right)_{HS} = \begin{cases} (1-\phi)^3/(1+2\phi) \approx 1 - 5\phi + 5\phi^2 & \text{in RP-PY} \\ 1 - 6.546\phi + 21.918\phi^2 + ? & \text{exact (Cichocki et al., '02)} \end{cases}$$



- near-field HI less important for sedimentation

- charged spheres :

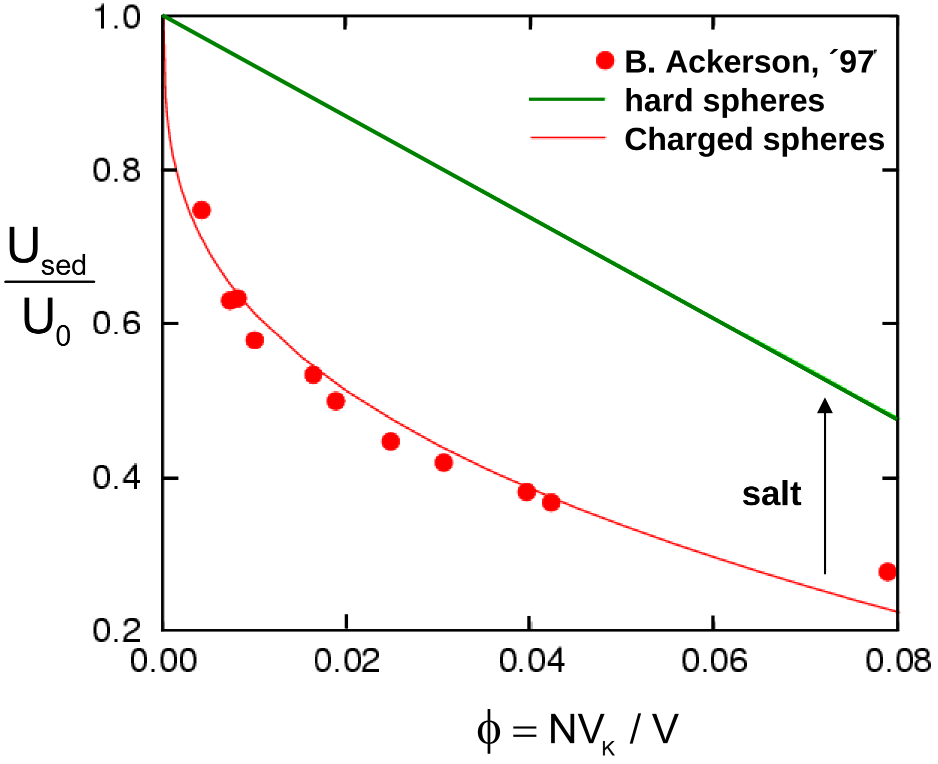
(Nägele & Watzlawek, PRE ´97)

$$\boxed{U_{sed} / U_0 \approx 1 - 1.8\phi^{1/3}}$$

- neutral hard spheres :

(Batchelor ´72, Cichocki et al. ´02)

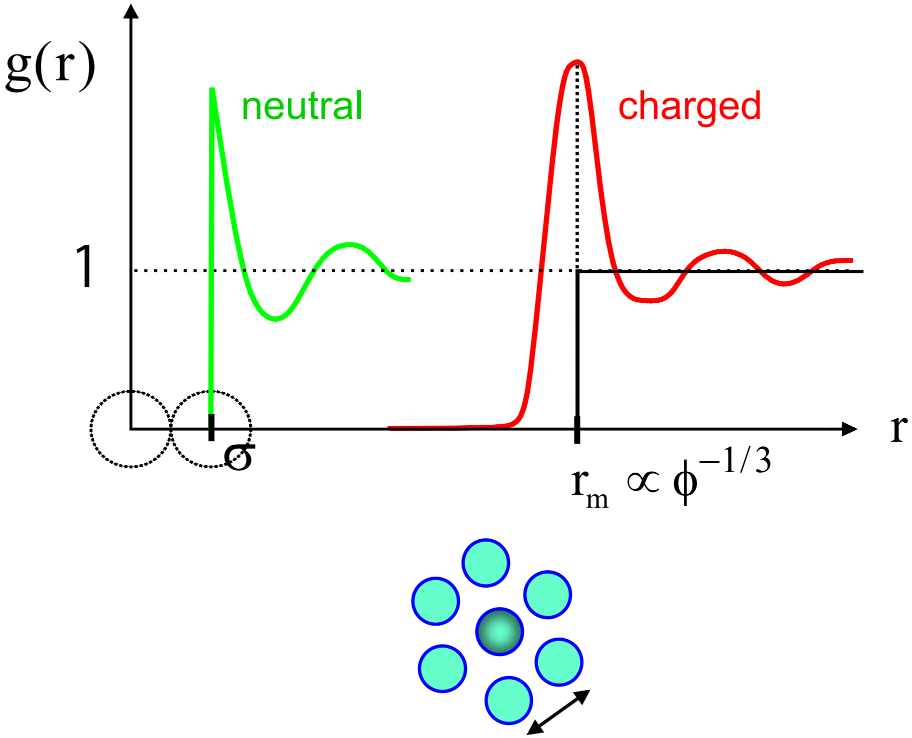
$$\boxed{U_{sed} / U_0 \approx 1 - 6.55\phi + 21.92\phi^2}$$



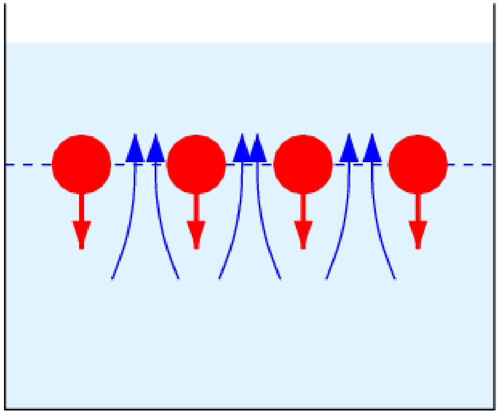
- charged particles sediment more slowly (sweet-water river delta)

- Charged colloids : non-linear density-dependence of transport coeff.

Radial distribution function



Solvent backflow



- Rough model of effective hard spheres :

$$g(r) \approx \Theta(r - \sigma_{\mathrm{eff}}) \qquad \sigma_{\mathrm{eff}} = r_{\mathrm{m}} \propto \phi^{-1/3}$$

$$\frac{U_{\mathrm{sed}}}{U_0} \approx 1 + \phi\left[-6\left(\frac{\sigma_{\mathrm{eff}}}{\sigma}\right)^2 + \ldots\right] \approx 1 - 6\,\phi^{1/3}$$

Oseen point-force approx.

# Smoluchowski equation with incident fluid flow

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

- Force balance in presence of incident flow $\mathbf{u}_0$ compatible with homog. Stokes eqs.
- Assume hydrodynamically torque-free spheres

$$\mathbf{v}_i - \mathbf{v}_{ic}(X;[\mathbf{u}_0]) = -\beta\sum_{l=1}^{N}\mathbf{D}^{tt}_{il}(X)\cdot\left[\mathbf{F}^{H}_{l} = -\mathbf{F}^{p}_{l} - \mathbf{F}^{ext}_{l} - \mathbf{F}^{B}_{l}\right]$$

indep. of $\mathbf{u}_0$

velocity of force- and torque-free sphere i advected by surrounding fluid (linear functional of $\mathbf{u}_0$)

$$\mathbf{v}_{ic} = \mathbf{u}_0(\mathbf{r}_i) + \int d\mathbf{r}'\,\mathbf{C}^{(k)}_{i}(\mathbf{r}';X)\cdot\mathbf{u}_0(\mathbf{r}') = \mathbf{u}_0(\mathbf{r}_i) + \mathbf{C}_i(X):\mathbf{e}_0$$

convection kernel

linear flow

3rd rank shear mobility tensor: $O(r^{-3})$

$$\frac{\partial}{\partial t}P(X,t) = \sum_{i,j=1}^{N}\nabla_i\cdot\mathbf{D}_{ij}\cdot\left[\nabla_j - \beta\mathbf{F}^{p}_{j}\right]P - \underbrace{\sum_{i,j=1}^{N}\nabla_i\cdot\mathbf{D}_{ij}\cdot\left[\beta\,\mathbf{F}^{ext}_{j}\,P\right]}_{\text{drift term (e.g. gravity)}} - \underbrace{\sum_{i=1}^{N}\nabla_i\cdot\left[\mathbf{v}_{ic}\,P\right]}_{\text{convective term}}$$

- Convective term vanishes in constant flow field $\mathbf{v}_B$ for homogeneous system
- Mere system translation with constant velocity does not affect Pdf („Galilei“-invariance)

$$\sum_{i=1}^{N}\nabla_i\cdot\left[\mathbf{v}_B\,P\right]=\mathbf{v}_B\cdot\sum_{i=1}^{N}\nabla_i\cdot P\underbrace{=}_{\substack{\uparrow\\ \text{translationally invariant system}}}0$$

- Application: uniform backflow does not change form of stationary homogeneous Pdf

$$\frac{\partial}{\partial t}P(X,t)=\left(\hat{O}+\hat{O}_{ad}\right)P(X,t)$$

$$\hat{O}_{adv}=-\nabla\bullet\mathbf{v}_c(X)$$

$$\hat{O}^{\dagger}_{adv}=\nabla\bullet\mathbf{v}_c(X)$$

- Flow-perburted (advective) part of Smoluchowski-op. not self-adjoint w/r to < | > , contrary to the unperturbed part

# Collective and gradient diffusion

$$\frac{\partial}{\partial t}S(q,t) = \underbrace{-\ q^2 D_0 \frac{H(q)}{S(q)} S(q,t)}_{\tau_B \ll t \ll \tau_I} \ + \underbrace{\int_0^t du\, M_c(q,t-u)\frac{S(q,u)}{S(q)}}_{t \gg \tau_I \quad \text{cage relaxation}}$$

$$M_c(t) = \left\langle f_{\mathbf{q}}^c \,|\, e^{\hat{Q}_c \hat{O}_B^0 \hat{Q}_c t} f_{\mathbf{q}}^c \right\rangle$$

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

$$D_C^S(q) := D_0 \frac{H(q)}{S(q)}$$

$$\boxed{D_C^S = \lim_{q\to 0}\frac{H(q)}{S(q)}}$$

short-time collective diffusion coefficient

$$\boxed{\exp\left\{-q^2 D_C^L\right\} = \lim_{t\to\infty}\lim_{q\to 0}\frac{S(q,t)}{S(q)}} \quad (q^2 t = O(1))$$

long-time collective or gradient diffusion coeff.

hydrodynamic limit

---

$$f_{\mathbf{q}}^c = i\mathbf{q}\cdot\frac{1}{\sqrt{N}}\underbrace{\sum_{i=1}^N \mathbf{v}_i^I}_{} + O(q^2) \quad \Rightarrow \quad \lim_{q\to 0}\frac{1}{q^2}M_C(q,t) = 0$$

zero mean drift velicity
for pairwise-addtive DI & HI
(no external force)

$$\boxed{D_C^S = D_L^S}$$

pairwise-addtive DI & HI

- Green-Kubo relation from memory eq. & definition of gradient diffusion coefficient :

$$D_c^L = D_c^S - \lim_{q\to\infty} \frac{1}{S(q)} \int_0^\infty dt \left\langle j_{\mathbf{q}}^c \,|\, e^{\hat{Q}_c \hat{O}_B^0 \hat{Q}_c t}\, j_{\mathbf{q}}^c \right\rangle$$

$$j_{\mathbf{q}}^c = \frac{1}{iq} O_0^B \, c_{\mathbf{q}}$$

Fourier-comp. of microscop. density fluctuations

- Comparison with Green-Kubo relation for $U_{sed}$ shows that :

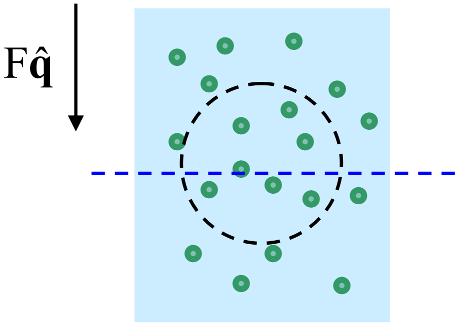
$$\boxed{\frac{D_c^L}{D_c^S} = \frac{U_{sed}^L}{U_{sed}^S}} \qquad D_c^L = \frac{D_0}{S(0)} \frac{U_{sed}^L}{U_0}$$

---

- Macroscopic phenomenological “derivation” from zero total flux balance in steady-state :

$$0 = \mathbf{j}_{sed} + \mathbf{j}_{diff} = \rho_0 U_{sed}^L \hat{\mathbf{q}} \; - \; D_C^L \nabla\rho$$

$$\nabla\rho = \left(\frac{\partial\rho_0}{\partial p}\right)_{T,\mu_s} \qquad \nabla p = \beta S(0) \rho_0 F \hat{\mathbf{q}}$$



small gradients, osmotic equil.

pressure gradient due to container bottom

# Gradient diffusion

- Gradient diffusion: $q << q_m$

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

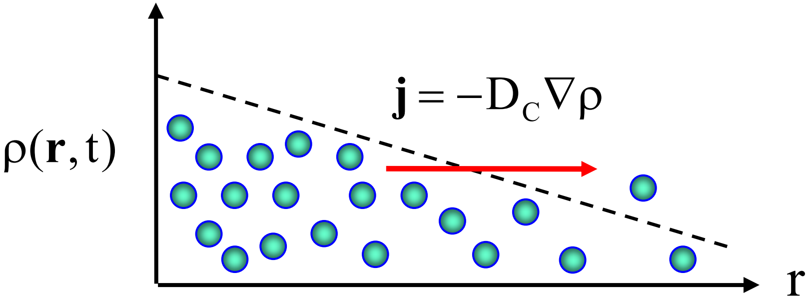
$$\boxed{\frac{D_C}{D_0} = \lim_{q \to 0} \frac{H(q)}{S(q)} = \frac{U_{sed} / U_0}{k_B T \left(\partial \bar{\rho} / \partial p\right)_T}}$$

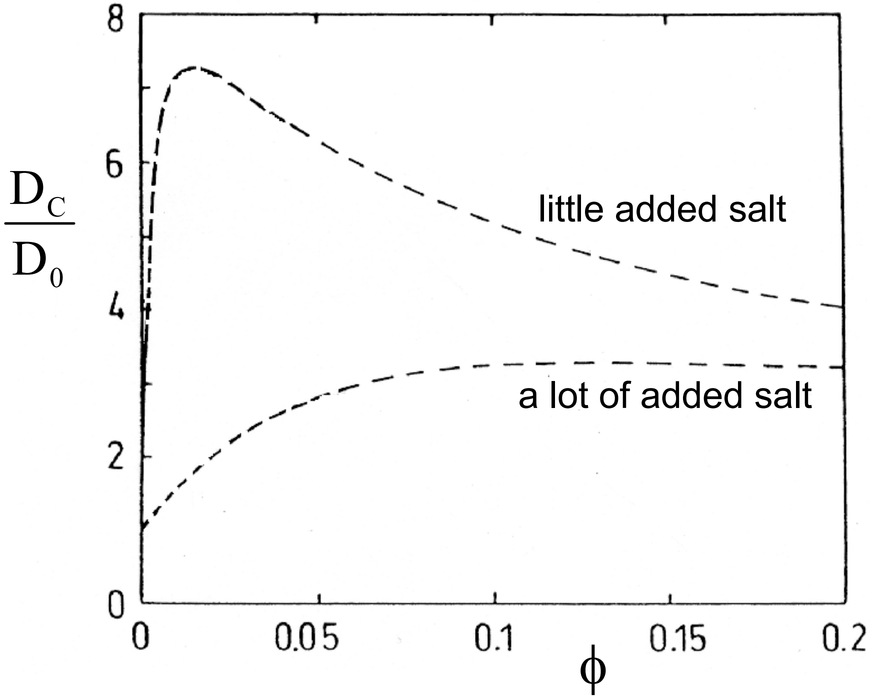
osmotic pressure

Hydrodynamic interaction : $U_{sed} / U_0$

⇕

Osmotic compressibility

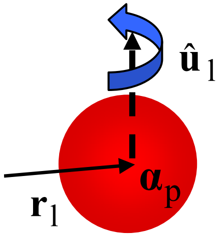


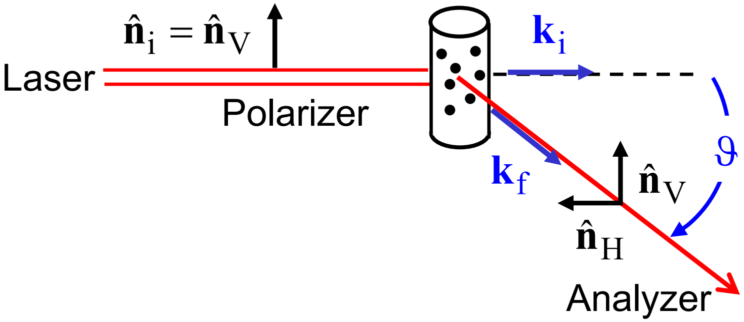


(G.N., Phys. Reports ´95)

# Rotational self-diffusion

Homogeneous spheres with single optical axis pointing along $\hat{\mathbf{u}}_1$





$$\mathbf{E}_S(\mathbf{q}) \propto \frac{e^{ik_i \cdot R}}{\lambda^2 R} \mathbf{E}_0 \sum_{l=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_l}\, \hat{\mathbf{n}}_f \cdot (\mathbf{1} - \hat{\mathbf{k}}_f \hat{\mathbf{k}}_f) \cdot \mathbf{B}_l(\mathbf{q}) \cdot \hat{\mathbf{n}}_i$$

$$\mathbf{B}_l(\mathbf{q}) \propto \left\{ \left(\alpha_p^{\|} - \alpha_s\right) \hat{\mathbf{u}}_l \hat{\mathbf{u}}_l + \left(\alpha_p^{\perp} - \alpha_s\right)\left(\mathbf{1} - \hat{\mathbf{u}}_l \hat{\mathbf{u}}_l\right) \right\}$$

$$\propto \left\{ \alpha \mathbf{1} + \beta \left( \hat{\mathbf{u}}_l \hat{\mathbf{u}}_l - \frac{1}{3} \mathbf{1} \right) \right\}$$

$\alpha = (\Delta\alpha_{||} + 2\Delta\alpha \perp)/3$

$\beta = \alpha_{||} - \alpha_{\perp}$ particle anisotropy (solvent-indep.)

From depolarized DLS in VH-geometry one determines electric field ACF :

$$g_E^{VH}(q,t) \propto \beta^2 G(q,t) G_r(t)$$

rotat.-transl. decoupling approx. for $t \sim \tau_I^r = 1/D_0^r$

$$G_r(t) = \left\langle P_2(\hat{\mathbf{u}}_1(t) \cdot \hat{\mathbf{u}}_1(0)) \right\rangle$$

$P_2(x) = \left(3x^2 - 1\right)/2$

rotational self-correlation function

- Hypothetical case : spheres interacting only by isotropic DI (no HI)

$$g_E^{VH}(q,t) \propto \beta^2 \left[ e^{-q^2 W(t)} \left(1 + \text{non-gaussian corr.}\right) \right] e^{-6 D_0^r t}$$

$$D_0^r = \frac{k_B T}{\zeta_0^r} = \frac{k_B T}{8\pi\eta_0 a^3}$$

independent spheres rotation

$$\left\langle \left[\hat{\mathbf{u}}(t) - \hat{\mathbf{u}}(0)\right]^2 \right\rangle_0 = 2\left[1 - e^{-2t/\tau_r}\right] = \left\{ \begin{array}{ll} 4 D_0^r t, & \tau_B^r \ll t \ll \tau_I^r \\ 2\ , & t \gg \tau_I^r \end{array} \right\}$$

$$\tau_B^r = \frac{(2/5)Ma^2}{\zeta_0^r} = \frac{3}{10}\tau_B$$

$$\tau_I^r = 1/D_0^r = (4/3)\tau_I$$

---

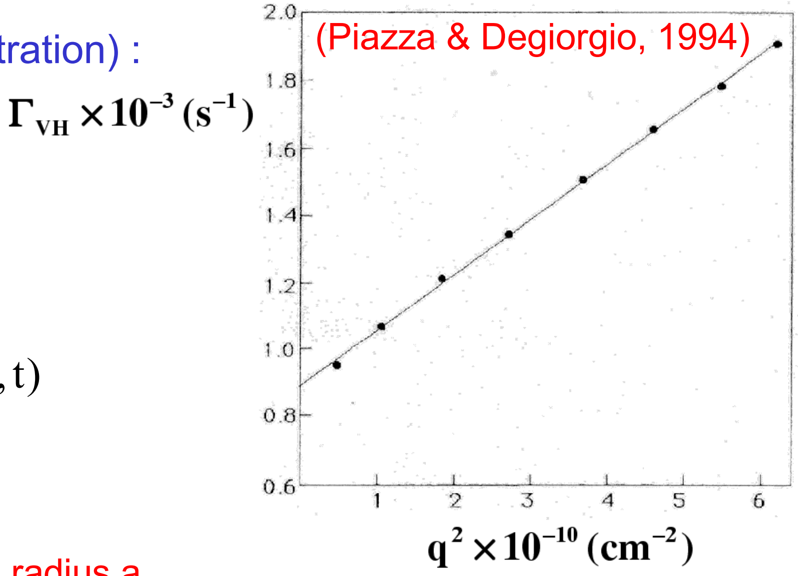
- Totally non-interacting spheres (very low concentration) :

$$g_E^{VH}(q,t) \propto \beta^2 \, e^{-\left(q^2 D_0 + 6 D_0^r\right)t}$$

- Initial decay rate : $\Gamma_{VH}(q) = -\lim_{t \to "0"} \frac{d}{dt} \ln g_E^{VH}(q,t)$

$$= \quad q^2 D_0 + 6 D_0^r$$

→ hydrodynamic sphere radius a



(Piazza & Degiorgio, 1994)

- Spheres with DI and HI : short-time rotational self-diffusion :

$$G_r(t) = e^{-6 D_s^r t} \, , \quad \tau_B^r \ll t \ll \tau_I^r \qquad\qquad D_S^r = -\frac{1}{6} \lim_{t \to 0} \frac{\partial \ln G_r(t)}{\partial t} \leq D_0^r$$

- From Smoluchowski equation for spheres including rotational degrees of freedom :

$$\frac{\partial}{\partial t} P(\mathbf{r}^N, \mathbf{u}^N t) = \left[ \hat{O}^{tt}(\mathbf{r}^N, \mathbf{u}^N) + \hat{O}^{tr}(\mathbf{r}^N, \mathbf{u}^N) + \hat{O}^{rt}(\mathbf{r}^N, \mathbf{u}^N) + \hat{O}^{rr}(\mathbf{r}^N, \mathbf{u}^N) \right] P$$

$$\boxed{D_S^r = \left\langle \hat{\mathbf{q}} \cdot \mathbf{D}_{11}^{rr}(\mathbf{r}^N) \cdot \hat{\mathbf{q}} \right\rangle_{eq}} \qquad\qquad \begin{pmatrix} \mathbf{v} \\ \boldsymbol{\omega} \end{pmatrix} = \beta \begin{pmatrix} \mathbf{D}^{tt}(X) & \mathbf{D}^{tr}(X) \\ \mathbf{D}^{rt}(X) & \mathbf{D}^{rr}(X) \end{pmatrix} \cdot \begin{pmatrix} \mathbf{F} \\ \mathbf{T} \end{pmatrix}$$

---

$$\boldsymbol{\omega}_1 = \beta \mathbf{D}_{11}^{rr}(X) \cdot \mathbf{T}_1 \, , \quad (\mathbf{F}_j = 0 = \mathbf{T}_j \text{ for } j \neq 1)$$

$$\mathbf{T}_i^H = -8\pi\eta_0 a^3 \left[ \boldsymbol{\omega}_i - \frac{1}{2} \nabla_i \times \left( \mathbf{u}_{N-1}(\mathbf{r}_i ; X) + \mathbf{u}_0(\mathbf{r}_i) \right) \right]$$

generalized rotational Faxén law (stick BCs)

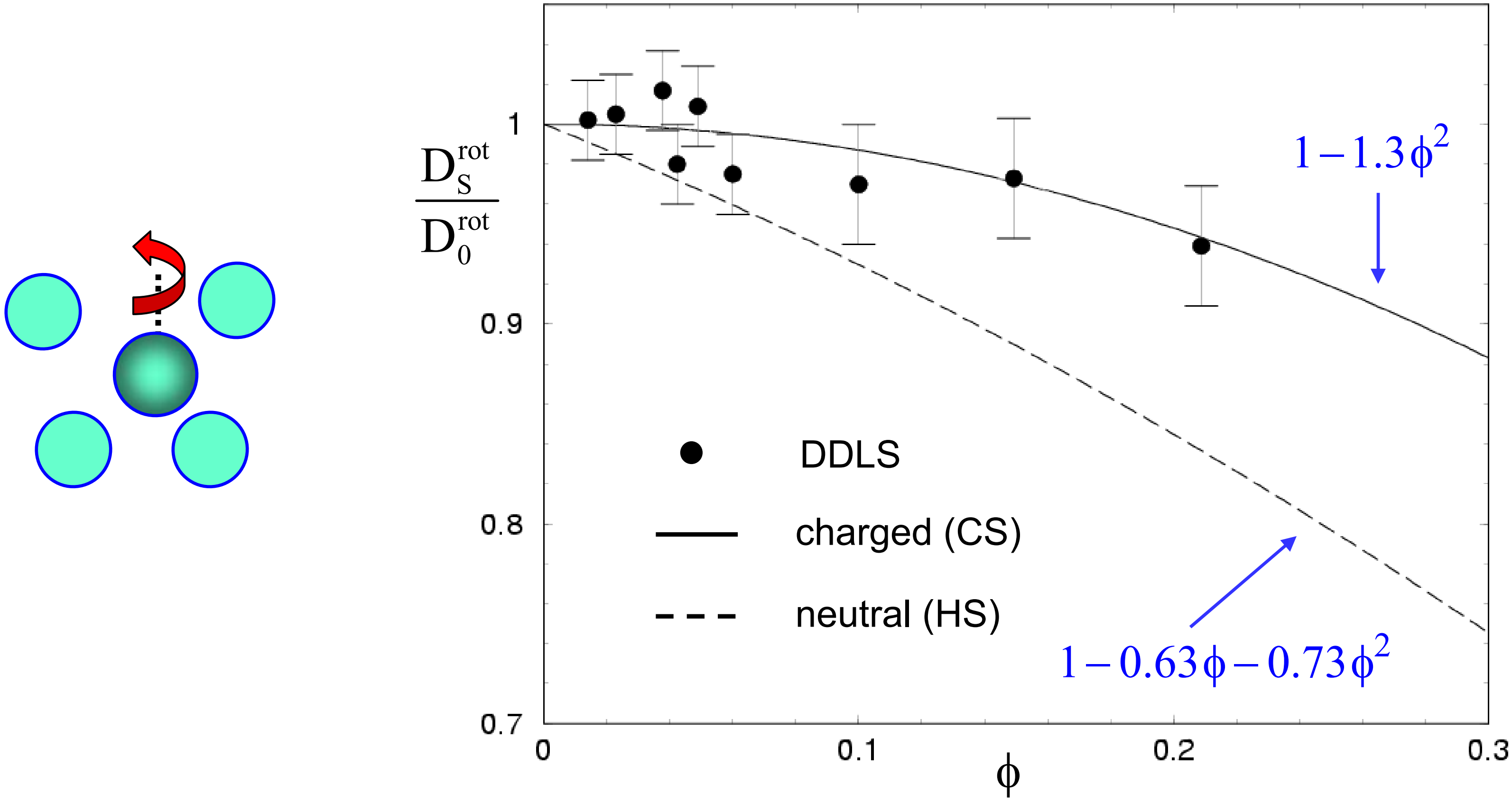
$$\mathbf{D}_{11}^{rr}(\mathbf{r}^N) = D_0^r \mathbf{1} + \underbrace{\Delta \mathbf{D}_{11}^{rr(2)}(\mathbf{r}^N)}_{\text{2-body HI}} + \underbrace{\Delta \mathbf{D}_{11}^{rr(3)}(\mathbf{r}^N)}_{\text{3-body HI}} + \ldots$$

$$\Delta\mathbf{D}_{11}^{rr(2)}(\mathbf{r}^N) = D_0^r \sum_{1\neq j}^{N} \boldsymbol{\omega}_{11}^{rr}(\mathbf{r}_{1j}) \qquad \Delta\mathbf{D}_{11}^{rr(3)}(\mathbf{r}^N) = O(r^{-9})$$

Long-distance multipole expansion of 2-body HI :

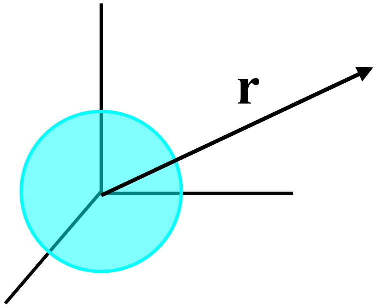
$$\boldsymbol{\omega}_{11}^{rr}(\mathbf{r}) = \underbrace{-\frac{15}{4}\left(\frac{a}{r}\right)^6}_{\text{first self-reflection}} \left[\mathbf{1} - \hat{\mathbf{r}}\hat{\mathbf{r}}\right] + O\left(r^{-8}\right)$$

# Charged spheres versus hard spheres



- DDLS: Bitzer, Palberg & Leiderer (Konstanz, ´97)
- CS with 3-body HI: Nägele, Watzlawek & Zhang, Physica A ´97 & JCP ´02
- HS with 3-body HI: Cichocki et al., JCP ´99

- Flow field $\mathbf{u}_0(\mathbf{r})$ of single sphere in origin with transl. velocity $\mathbf{v}_0$ and rotat. velocity $\boldsymbol{\omega}_0$
- Stick BC on sphere surface and quiescent unbound fluid



$$\mathbf{u}(\mathbf{r})\Big|_{r\geq a} = \underbrace{\left[\frac{3}{4}\left(\frac{a}{r}\right)\left(\mathbf{1}+\hat{\mathbf{r}}\,\hat{\mathbf{r}}\right)+\frac{1}{4}\left(\frac{a}{r}\right)^3\left(\mathbf{1}-3\hat{\mathbf{r}}\,\hat{\mathbf{r}}\right)\right]}_{\zeta_0\left(\mathbf{1}+\frac{a^2}{6}\nabla^2\right)\mathbf{T}_0(\mathbf{r})}\cdot\mathbf{v}_0+\left(\frac{a}{r}\right)^3\boldsymbol{\omega}_0\times\mathbf{r}$$

$$\mathbf{u}(\mathbf{r})\Big|_{r=a} = \mathbf{v}_0+\omega_0\times\left(a\,\hat{\mathbf{r}}\right)$$

# 8. Long-time dynamics

- Generalized hydrodynamics
- Mode coupling approximation of memory functions
- Application: non-exponential decay of dynamic structure factor

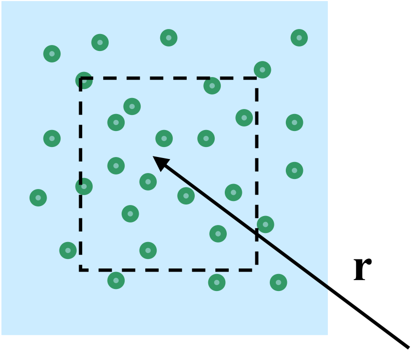
# Generalized hydrodynamics

- Phenomenological starting point :

$$\frac{\partial}{\partial t}\bar{\rho}(\mathbf{r},t)+\nabla\cdot\bar{\mathbf{j}}(\mathbf{r},t)=0 \qquad \bar{\rho}(\mathbf{r},t)=\frac{1}{\Delta V}\int d\mathbf{x}\,\rho(\mathbf{x},t)$$

$$\bar{\mathbf{j}}(\mathbf{r},t)=-\int_0^t dt'\int d\mathbf{r}\,\mathbf{D}_c(|\mathbf{r}-\mathbf{r}'|,t-t')\cdot\nabla'\bar{\rho}(\mathbf{r}',t')$$

$$S(q,t)=\frac{V}{N}\int d(\mathbf{r}'-\mathbf{r})e^{i\mathbf{q}\cdot(\mathbf{r}'-\mathbf{r})}\langle\bar{\rho}(\mathbf{r}',0)\bar{\rho}(\mathbf{r},t)\rangle$$



$$\Delta x\gg\sqrt{D_0\tau_B}$$

$$\Delta t\gg\tau_B$$

→

$$\tilde{S}(q,z)=\int_0^\infty dt\,e^{-zt}S(q,t)=\frac{S(q)}{z+q^2\tilde{D}_c(q,z)}$$

$$\tilde{D}_c(q,z)=\int_0^t dt\,e^{-zt}\int d\mathbf{r}\,e^{i\mathbf{q}\cdot\mathbf{r}}\,\hat{\mathbf{q}}\cdot\mathbf{D}_c(r,t)\cdot\hat{\mathbf{q}}\geq 0$$

spectrum of relaxation frequencies z

$$D_c^L=\tilde{D}_c(q\to 0,z\to 0)\quad\longleftrightarrow\quad S(q\ll q_m,t\gg\tau_I)\propto\exp\left\{-q^2\,D_c^L\,t\right\}$$ hydrodyn. limit

$$D_c^S(q)=\tilde{D}_c(q,z\to\infty)\quad\longleftrightarrow\quad S(q,t\ll\tau_I)\propto\exp\left\{-q^2\,D_c^S(q)\,t\right\}$$ short-time limit

- Split $\tilde{D}_c^L(q,z)$ in instantaneous & relaxational part :

$$\tilde{D}_c(q,z) = D_0 \frac{H(q)}{S(q)} - \frac{\tilde{M}(q,z)}{q^2 S(q)} \geq 0$$

$$\boxed{\frac{\partial}{\partial t} S(q,t) = - \underbrace{q^2 D_0 \frac{H(q)}{S(q)}}_{=:1/\tau_S(q)} S(q,t) + \int_0^t du\, M_c(q,t-u) \frac{S(q,u)}{S(q)}}$$

approximation of $M_c$ might violate positivity for strong coupling

---

- Define generalized friction kernel function $\tilde{\zeta}_c(q,z)$ through :

$$\tilde{\zeta}_c(q,z) = \frac{k_B T / S(q)}{\tilde{D}_c(q,z)} \longrightarrow \zeta_0 = \frac{k_B T}{D_0} \qquad (\rho \to 0)$$

- Again, split in instantaneous and relaxational part :

$$\tilde{\zeta}_c(q,z) = \frac{\zeta_0}{H(q)} + \Delta\tilde{\zeta}_c(q,z)$$

- Define so-called irreducible memory function by :

$$\tilde{m}_c^{irr}(q,z) = \frac{H(q)}{\zeta_0} \Delta\tilde{\zeta}_c(q,z)$$

$$\tilde{S}(q,z) = \frac{S(q)}{z + \frac{\tau_s(q)^{-1}}{1 + \tilde{m}_c^{irr}(q,z)}} \longleftrightarrow \boxed{\frac{\partial}{\partial t} S(q,t) = - \frac{1}{\tau_s(q)} S(q,t) - \int_0^t du\, m_c^{irr}(q,t-u) \frac{\partial S(q,u)}{\partial u}}$$

renormalizes short-time lifetime of density fluctuations

- best suited for memory approximations
- can preserve positivity of $\tilde{D}_c(q,z)$

# Mode coupling approximation of memory functions

- Microscopic expression for irreducible memory function : Nägele & Baur, Physica A (1997)

$$m_c^{irr}(q,t) = \frac{1}{q^2 D_0 H(q)} \underbrace{\left\langle f_{\mathbf{q}}^c \,|\, e^{\hat{\Omega}_c^{irr}\, t} f_{\mathbf{q}}^c \right\rangle}_{=:\, M_c^{irr}(q,t)}$$

$$\hat{\Omega}_c^{irr} = \hat{Q}_c \left[ \hat{O}_B + \frac{1}{q^2 D_0 H(q)} \left| f_{\mathbf{q}}^c \right\rangle \left\langle f_{\mathbf{q}}^c \right| \right] \hat{Q}_c$$

irreducible Smoluchowski op.
for collective diffusion

- for comparison :

$$M_c(q,t) = \left\langle f_{\mathbf{q}}^c \,|\, e^{\hat{Q}_c \hat{O}_B^0 \hat{Q}_c\, t} f_{\mathbf{q}}^c \right\rangle$$

$$M_c^{un}(q,t) = \left\langle f_{\mathbf{q}}^c \,|\, e^{\hat{O}_B^0\, t} f_{\mathbf{q}}^c \right\rangle$$

← unreduced force-force ACF

- Relations among various force ACFs :

$$\tilde{M}_c(q,z) = \frac{\tilde{m}_c^{irr}(q,z)}{1+\tilde{m}_c^{irr}(q,z)} = \tilde{M}_c^{un}(q,z) \left[ 1 + \frac{\tilde{M}_c^{un}(q,z)}{z\, S(q) + q^2 D_0 H(q)} \right]^{-1}$$

- Provided ACFs are expandable in smallness parameter $\varepsilon$ and are of $O(\varepsilon)$ :

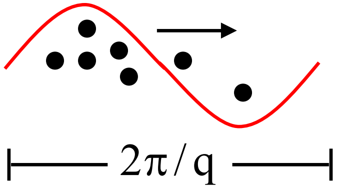
$$M(q,t) = M_c^{irr}(q,t) = M_c^{un}(q,t) + O(\varepsilon^2)$$

Example: $\varepsilon = u(r)^2$, $\rho$

# Lowest order mode coupling approximation

$$\frac{\partial}{\partial t} c_{\mathbf{q}} \equiv \hat{O}_B c_{\mathbf{q}} = i\mathbf{q} \cdot \mathbf{j}_{\mathbf{q}}^{c} \to 0 \quad , \; q \to 0$$

slow, at least for q small



$A = c_{\mathbf{q}}$

- What about "slowness" of density products AA, AAA, ... ?

- Basic idea : - project $f_{\mathbf{q}}$ into sub-subspace of slowest of fast variables spanned by binary products of density fluctuations

  - expected to dominate long-time decay of $M_c^{irr}(q,t)$ at least for dense systems with strong caging

---

- Introduce projector on bilinear density variables :

$$P_{\mathbf{q}}^{(2)} \equiv \sum_{\mathbf{k}} \frac{\left| c_{\mathbf{q}-\mathbf{k}}\, c_{\mathbf{k}} \right\rangle \left\langle c_{\mathbf{k}}\, c_{\mathbf{q}-\mathbf{k}} \right|}{2\, S(k)\, S(|\, \mathbf{q} - \mathbf{k}\, |)}$$

- 1. Approximation : $e^{\hat{\Omega}_c^{irr}\, t} \approx P_{\mathbf{q}}^{(2)}\, e^{\hat{\Omega}_c^{irr}\, t}\, P_{\mathbf{q}}^{(2)}$

$$m_c^{irr}(q,t) \propto \frac{1}{4q^2}\sum_{\mathbf{k},\mathbf{k}'}\frac{\left\langle f_{\mathbf{q}}^c \middle| c_{\mathbf{q}-\mathbf{k}}\, c_{\mathbf{k}}\right\rangle \left\langle c_{\mathbf{k}'}\, c_{\mathbf{q}-\mathbf{k}'} \middle| f_{\mathbf{q}}^c\right\rangle}{S(k)\,S(k')\,S(|\mathbf{q}-\mathbf{k}|)\,S(|\mathbf{q}-\mathbf{k}'|)}\underbrace{\left\langle c_{\mathbf{k}}\, c_{\mathbf{q}-\mathbf{k}} \,\middle|\, e^{\hat{\Omega}_c^{irr} t}\, c_{\mathbf{q}-\mathbf{k}'}\, c_{\mathbf{k}'}\right\rangle}_{\Big\downarrow}$$

$$\approx S(k,t)\,S(|\mathbf{q}-\mathbf{k}|,t)\left[\delta_{\mathbf{k}',\mathbf{k}} + \delta_{\mathbf{k}',\mathbf{q}-\mathbf{k}}\right]$$

- 2. Approximation : → use Gaussian factorization of 4-point corr. function

→ replace $\exp\left\{\hat{\Omega}_c^{irr} t\right\}$ by $\exp\left\{\hat{O}_B t\right\}$

- MCT result for $m_c^{irr}(q,t)$ with HI neglected (Götze, Fuchs et al., Szamel & Löwen) :

$$\boxed{m_c^{irr}(q,t) = \frac{\rho D_0}{2(2\pi)^3}\int d\mathbf{k}\left[V_c(\mathbf{q},\mathbf{k})\right]^2 S(k,t)\,S(|\mathbf{q}-\mathbf{k}|,t) \geq 0}$$

$$V_c(\mathbf{q},\mathbf{k}) = \hat{\mathbf{q}}\cdot\mathbf{k}\, c(k) + \hat{\mathbf{q}}\cdot(\mathbf{q}-\mathbf{k})\, c(|\mathbf{q}-\mathbf{k}|) + q\rho\, c^{(3)}(\mathbf{k},\mathbf{q}-\mathbf{k})$$

usually neglected
(convolution approx.)

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

→ single static input required is : S(q) = 1/(1 - ρc(q))

$$\delta\rho_{\mathbf{q}} = \sum_{l=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_l} - N\delta_{\mathbf{q},0} = \sqrt{N}\,c_{\mathbf{q}}$$

$$S^{(3)}(\mathbf{k},\mathbf{k}') \equiv \frac{1}{N}\left\langle \delta\rho_{\mathbf{k}}\,\delta\rho_{\mathbf{k}'}\,\delta\rho_{-\mathbf{k}-\mathbf{k}'} \right\rangle = \sqrt{N}\left\langle \delta c_{\mathbf{k}}\,\delta c_{\mathbf{k}'}\,\delta c_{-\mathbf{k}-\mathbf{k}'} \right\rangle$$

$$S^{(3)}(\mathbf{k},\mathbf{k}') \equiv S(k)S(k')S(|\mathbf{k}-k'|)\left[1+\rho^2 c^{(3)}(\mathbf{k},\mathbf{k}')\right] \approx S(k)S(k')S(|\mathbf{k}-k'|)$$

- Static convolution approximation (CA) :

  ⊖ does not vanish when centers of two particles coincide

  ⊕ becomes exact to linear order in $\rho$ and to linear order in $u(r)$ (WCA)

- MCT applied to irreducible memory function :

⊕ gives exact limit of weakly interacting point particles

⊕ preserves strict monotonicity of (irreducible) memory function

⊕ becomes exact for point particles to linear order in $u(r)$ (WCA)

⊕ correct functional short- and long-time asymptotics for HS w/o HI, including q-dependence

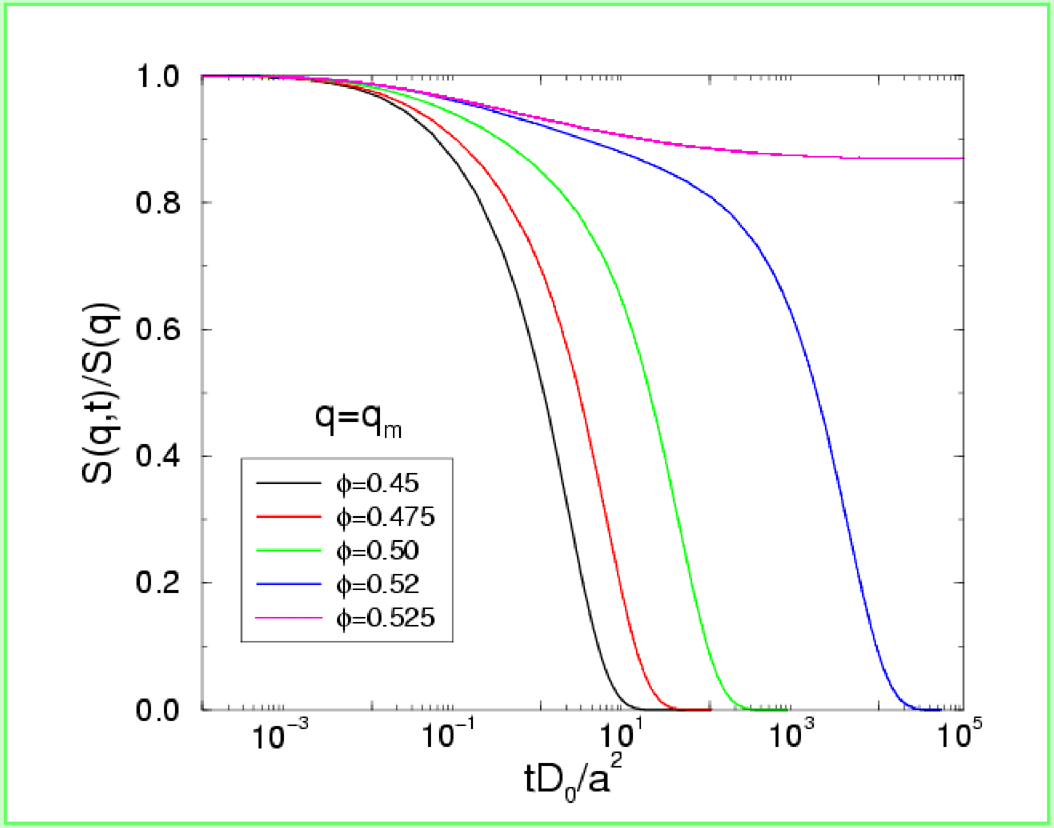
⊕ consistent idealized glass transition scenario

⊖ not exact at small times or densities

⊖ non-systematic approximation (no smallness parameter)

⊕ consistent idealized glass transition scenario

$$\frac{S(q,t\to\infty)}{S(q)} \to f_c(q) > 0 \qquad (\phi > \phi_g)$$



Hard spheres :

$$\phi_g^{exp} \approx 0.57$$

$$\phi_g^{MCT} \approx 0.525$$

# Extension: approximate inclusion of far-field HI on Rotne-Prager level

$$\hat{O}_B(\mathbf{r}^N) = \underbrace{D_0 \sum_{i=1}^{N} \left[\nabla_i + \beta\,\mathbf{F}_i^p\right]\cdot\nabla_i}_{\substack{\uparrow \\ \hat{O}_B^p(\mathbf{r}^N)}} + \underbrace{D_0 \sum_{i,j}^{N}{}'\,\mathbf{T}_{ij}^{RP}(\mathbf{r}_{ij}) : \left[\beta\,\mathbf{F}_i^p\,\nabla_j + \nabla_i\,\nabla_j\right]}_{\substack{\uparrow \\ \hat{O}_B^{hyd}(\mathbf{r}^N)}}$$

$$f_{\mathbf{q}}^{c} = f_{\mathbf{q}}^{c,p} + f_{\mathbf{q}}^{c,hyd}$$

$$\hat{\Omega}_c^{irr} = \hat{Q}_c\left[\hat{O}_B + \frac{1}{q^2\,D_0\,H(q)}\left|f_{\mathbf{q}}^{c}\right\rangle\left\langle f_{\mathbf{q}}^{c}\right|\right]\hat{Q}_c$$

→ use same 4-point factorization approximation

→ same static convolution approximation (needed for collective diffusion only)

→ extended to mixtures and linear viscoelasticity (Nägele et al., 1997 - 2000)

- Example: MCT with far-field HI for self-dynamic scattering function G(q,t) :

$$\frac{\partial}{\partial t} G(q,t) = -\, q^2 D_s G(q,t) - \int_0^t du\, m_s^{irr}(q,t-u)\, \frac{\partial G(q,u)}{\partial u}$$

$$m_c^{irr}(q,t) = \frac{1}{q^2 D_s} \left\langle f_{\mathbf{q}}^s \,|\, e^{\hat{\Omega}_s^{irr}\, t} f_{\mathbf{q}}^s \right\rangle$$

$$\hat{\Omega}_s^{irr} = \hat{Q}_s \left[ \hat{O}_B + \frac{1}{q^2 D_s} \left| f_{\mathbf{q}}^s \right\rangle \left\langle f_{\mathbf{q}}^s \right| \right] \hat{Q}_s$$

irreducible Smoluchowski op.
for self-diffusion

$$\hat{Q}_s = \mathbf{1} - \left| a_{\mathbf{q}} \right\rangle \left\langle a_{\mathbf{q}} \right|$$

- Apply MCT approximation with RP-HI :

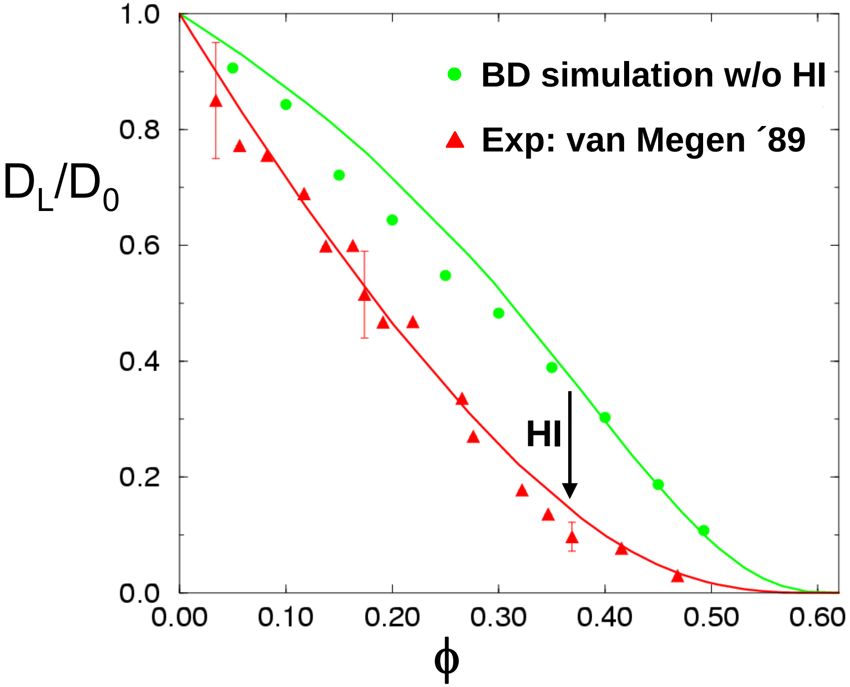
$$m_s^{irr}(q,t) = \frac{D_0}{2(2\pi)^3 \rho} \int d\mathbf{k} \left[ V_s(k) \right]^2 S(k,t)\, G(|\mathbf{q}-\mathbf{k}|,t) \geq 0$$

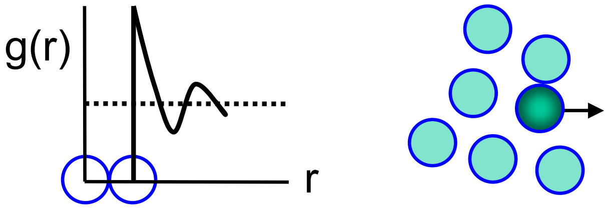
$$V_s(k) = \left[ 1 - \frac{H(k)}{S(k)} \right]$$

Input is now S(q) and H(q)

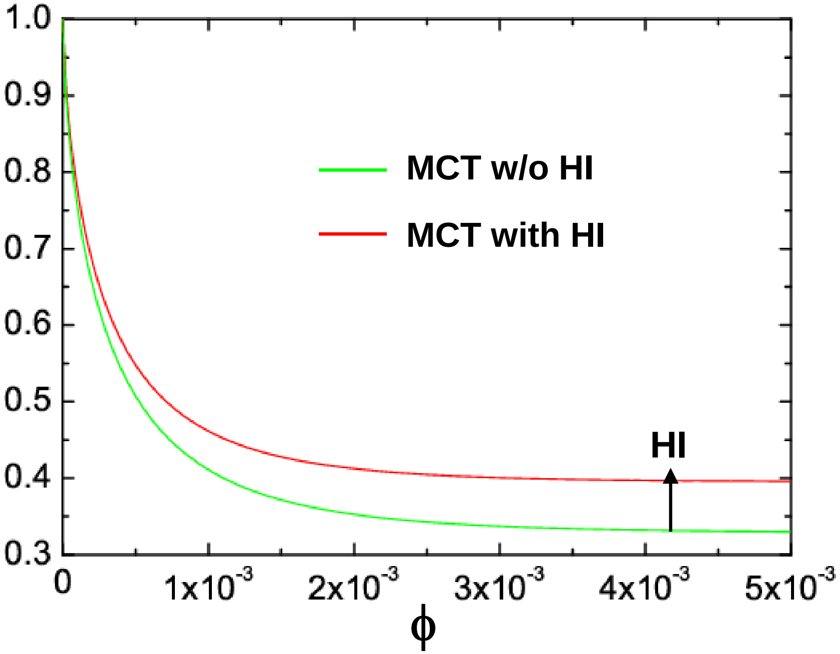
# MCT results for long-time self-diffusion

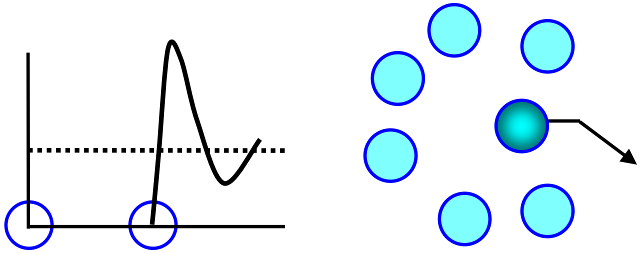
- hard spheres





- charged spheres





( G.N. & Banchio et al., Europhys. Lett. ´97 & JCP ´00 )

# VAF: general behavior

- From memory eq. for $G(q,t)=\exp[-q^2 W(t)]+O(q^4)$ follows :

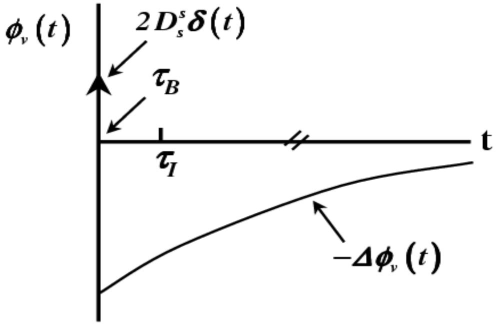
$$W(t)=D_s t-\int_0^t du\,(t-u)\left\langle \hat{\mathbf{q}}\cdot\mathbf{v}_1^I \,|\, e^{\hat{O}_B u}\,\hat{\mathbf{q}}\cdot\mathbf{v}_1^I\right\rangle \to D_L\, t \quad (t\gg\tau_I)$$

- Comparison with generally valid Ornstein-Fürth formula (requires only stationarity) :

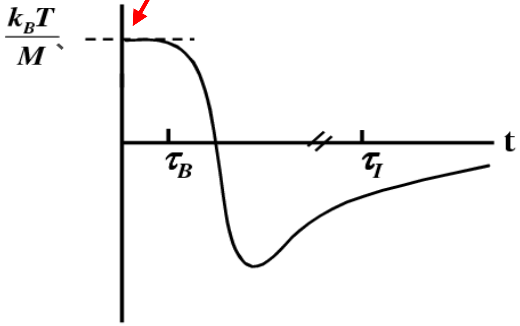
$$W(t)=\int_0^t du\,(t-u)\,\phi_v(u) \longrightarrow$$

$$\phi_v(t)=2D_S\delta(t)-\Delta\phi_v(t)$$

$$D_L=D_S-\int_0^\infty dt\,\Delta\phi_v(t)<D_S$$



except HS



$$\phi_v(t\gg\tau_m)\approx -A\left(\frac{t}{\tau_m}\right)^{-(d+2)/2}$$

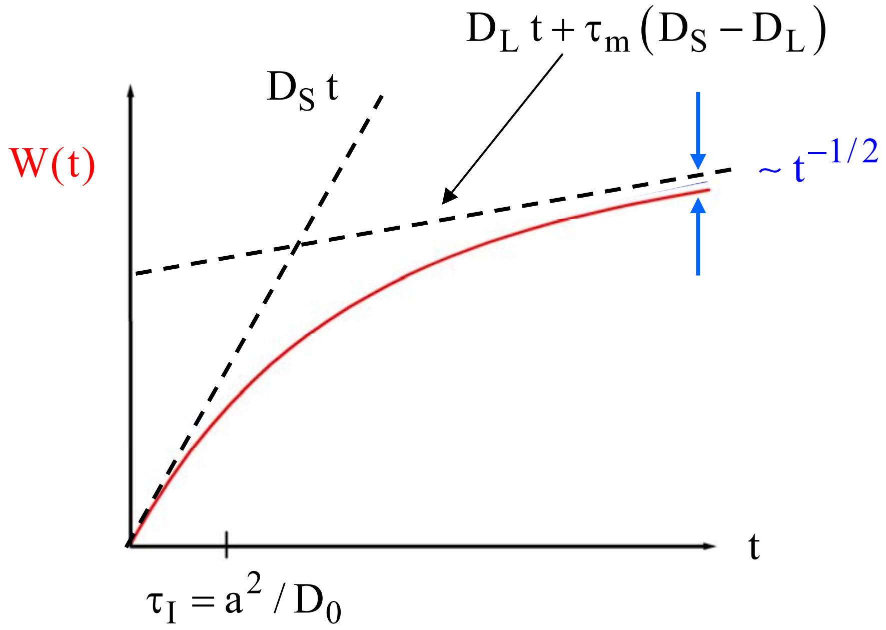
negative configurational long-time tail

# MSD: general behavior

$$W(t) = D_L t + \tau_m (D_s - D_L) - \int_t^{\infty} du\,(u - t)\,\Delta\phi_v(u)$$

$\tau_m$ : mean relaxation time of corresponding VAF (regular part)

$$\tau_m = \int_0^{\infty} dt\, t\, \Delta\phi_v(t) \bigg/ \int_0^{\infty} dt\, \Delta\phi_v(t)$$



(in 3D : HS + WCA)

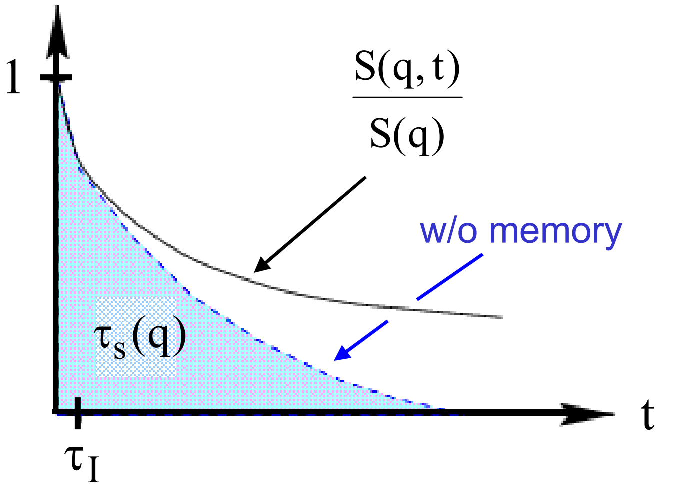
# Application: non-exponential decay of dynamic structure factor

- Global measure : non-exponentiallity factor

$$\boxed{\Delta(q) \equiv 1 - \frac{\tau_s(q)}{\overline{\tau}(q)}}$$

$$\overline{\tau}(q) = \int_0^\infty dt \, \frac{S(q,t)}{S(q)}$$

$$\tau_s(q) = \left( q^2 D_0 \frac{H(q)}{S(q)} \right)^{-1}$$



$\Delta(q) \ll 1$ : weakly non-exp.

$\Delta(q) \sim 1$ : strong non-exp.

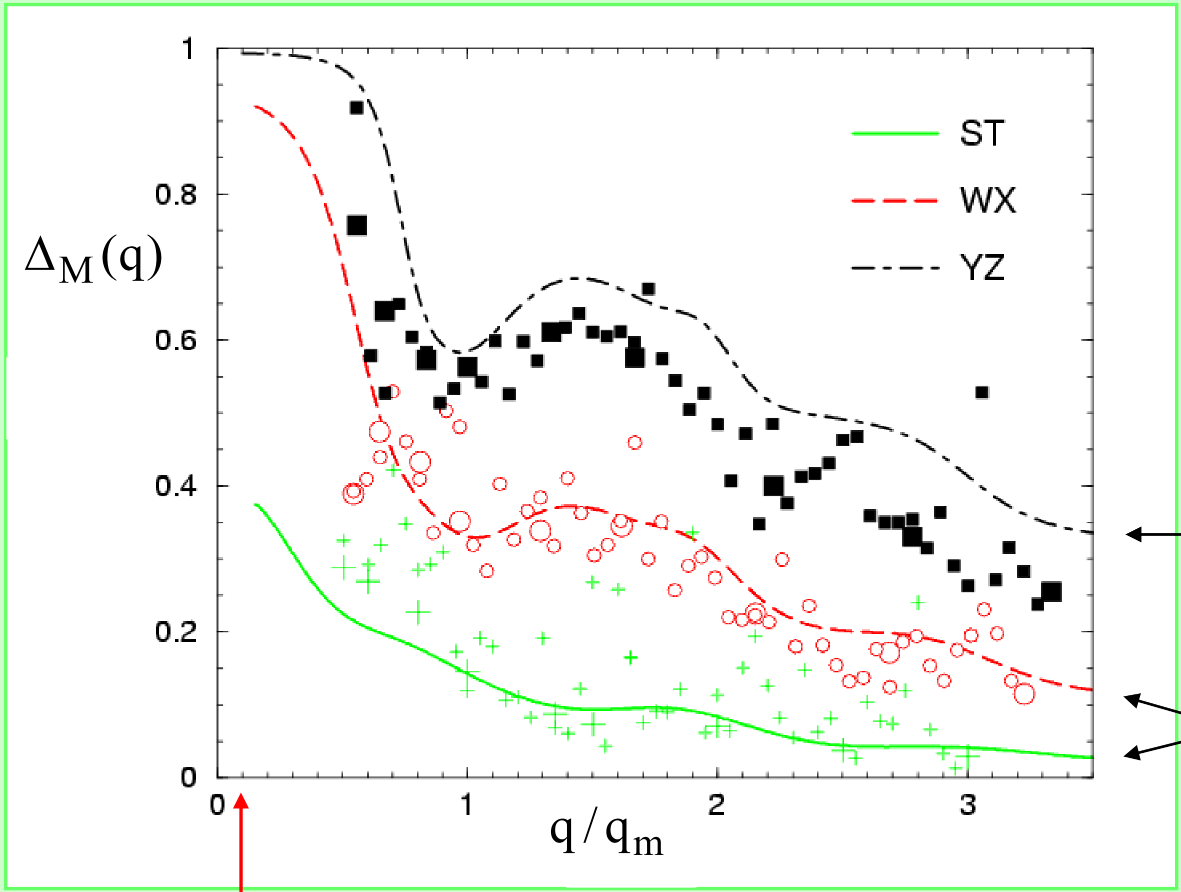
- from memory eqs. for S(q,t) follow :

$$\Delta(q) = \frac{\tilde{m}_c^{irr}(q, z=0)}{1 + \tilde{m}_c^{irr}(q, z=0)} = \frac{\tilde{M}_c(q,z)}{q^2 D_0 \, H(q)} \quad \longrightarrow \quad 0 \leq \Delta(q) \leq 1$$

$$\boxed{\lim_{q \to 0} \Delta(q) = \frac{D_c^S - D_c^L}{D_c^S}}$$

- zero for no or PA-HI
- smaller than 0.06 for dense hard-sphere systems

- Measured non-exponentiallity factor for charge-stabilized dispersions



$$\phi \sim 10^{-4} - 10^{-3}$$

$$s = \sqrt{\langle \sigma^2 \rangle - \overline{\sigma}^2} / \overline{\sigma} = 0.05$$

zero added salt

little added salt

$$\Delta(q \gg q_m) > 1 - D_L / D_S$$

**Puzzle :** - reason for strong „non-exponentiallity“ near q = 0 ?
- can‘t be due to many-body HI !

Exp.: Müller & Schätzel, Kiel (1993)
Theory: Banchio, Nägele & Bergenholtz, J. Chem. Phys. (2000)

- Resolution : tiny amount of size-polydispersity is sufficient

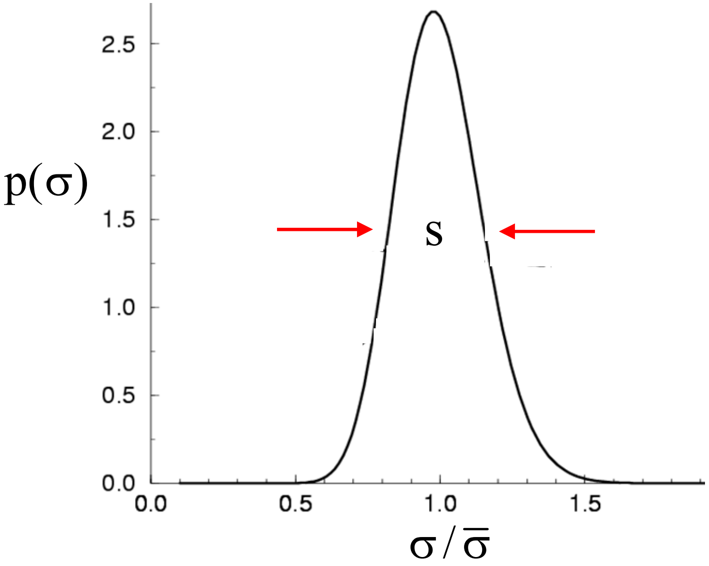
DLS-measurable dynamic structure factor for polydisperse system :

$$S_M(q,t) \propto \sum_{\alpha,\beta=1}^{m} (x_\alpha x_\beta)^{1/2} b_\alpha(q) b_\beta(q) S_{\alpha\beta}(q,t)$$

Small polydispersity $s \ll 1$ $\Rightarrow$ decoupling approx.

$$S_M(q,t) \propto X(q) G_{id}(q,t) + [1 - X(q)] S_{id}(q,t)$$

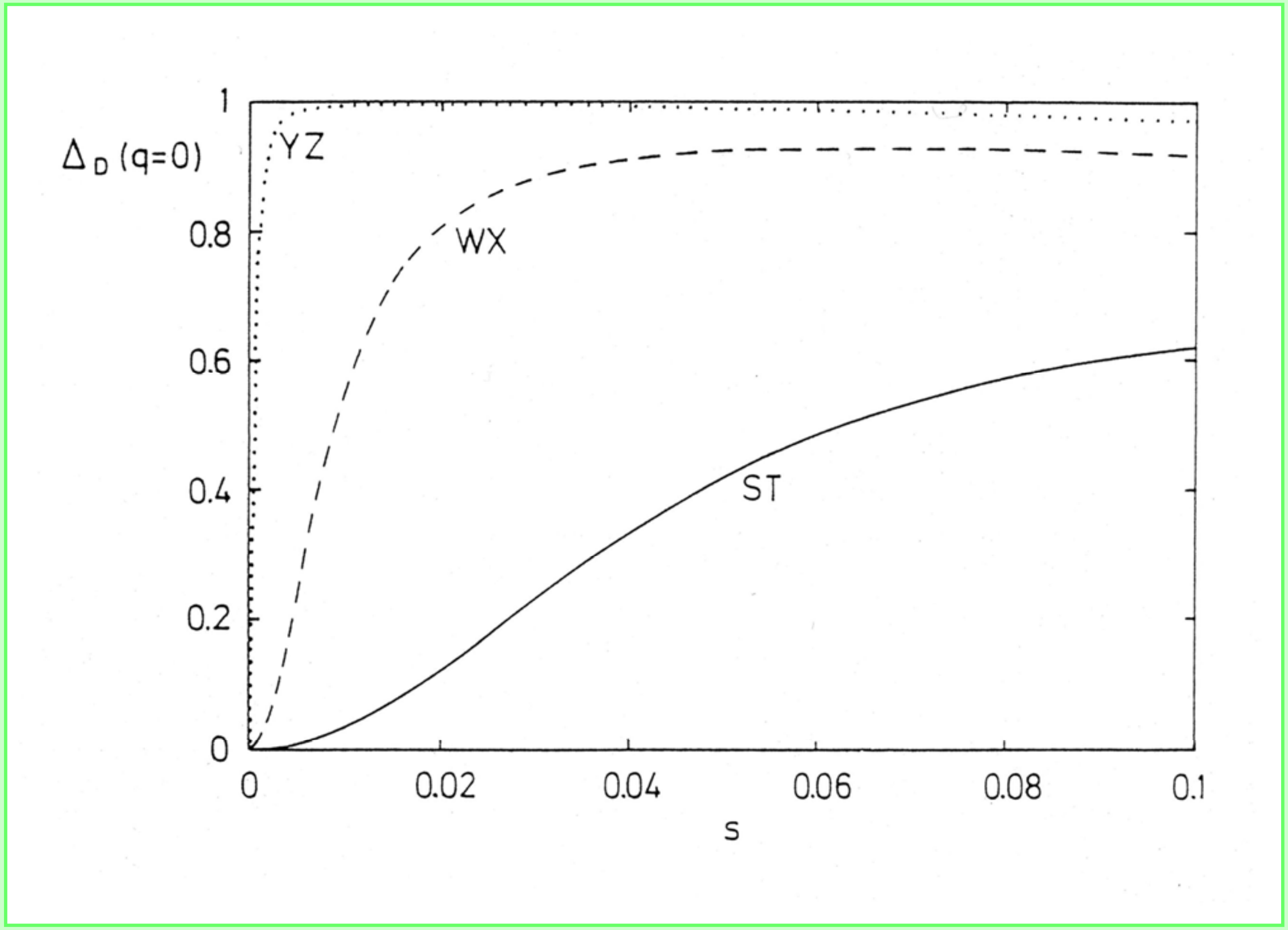
$$X(q) = 1 - \frac{\langle b(q) \rangle_p^2}{\langle b(q)^2 \rangle_p} \approx 9s^2 \qquad (q\sigma < 1.5)$$



$$\boxed{\Delta_M(q \to 0) = 1 - \frac{\tau_s^M(q)}{\overline{\tau}^M(q)} > 0}$$ since :

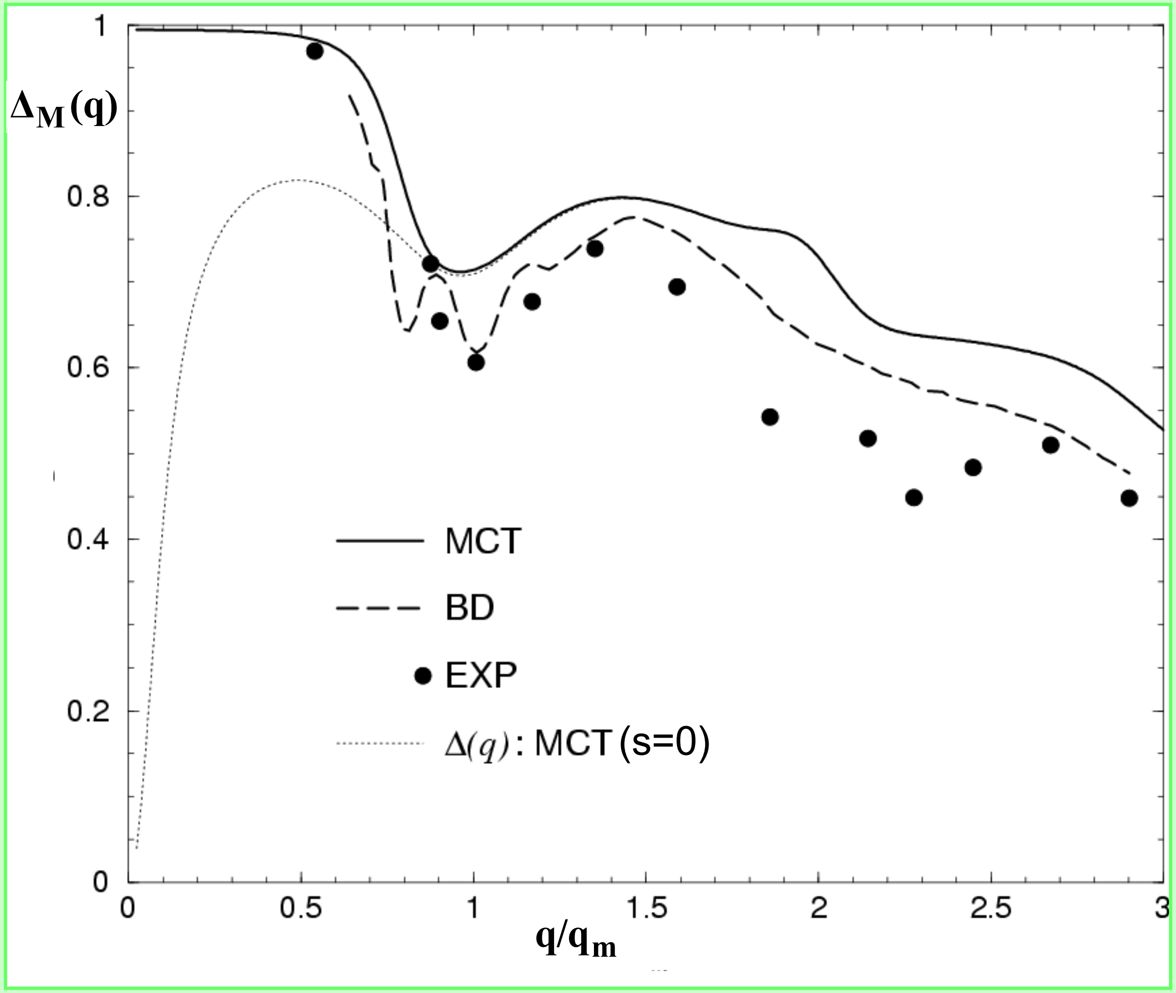
$$S_M(q \ll q_m, t) \propto (1 - 9s^2) \underbrace{S(0)}_{\ll 1} \underbrace{\exp\left\{-q^2 D_0 \frac{H(0)}{S(0)} t\right\}}_{\text{decays fast}} + 9s^2 \underbrace{\exp\left\{-q^2 W(t)\right\}}_{\text{decays slowly}}$$

- Influence of polydispersity s on $\Delta_M(q=0)$



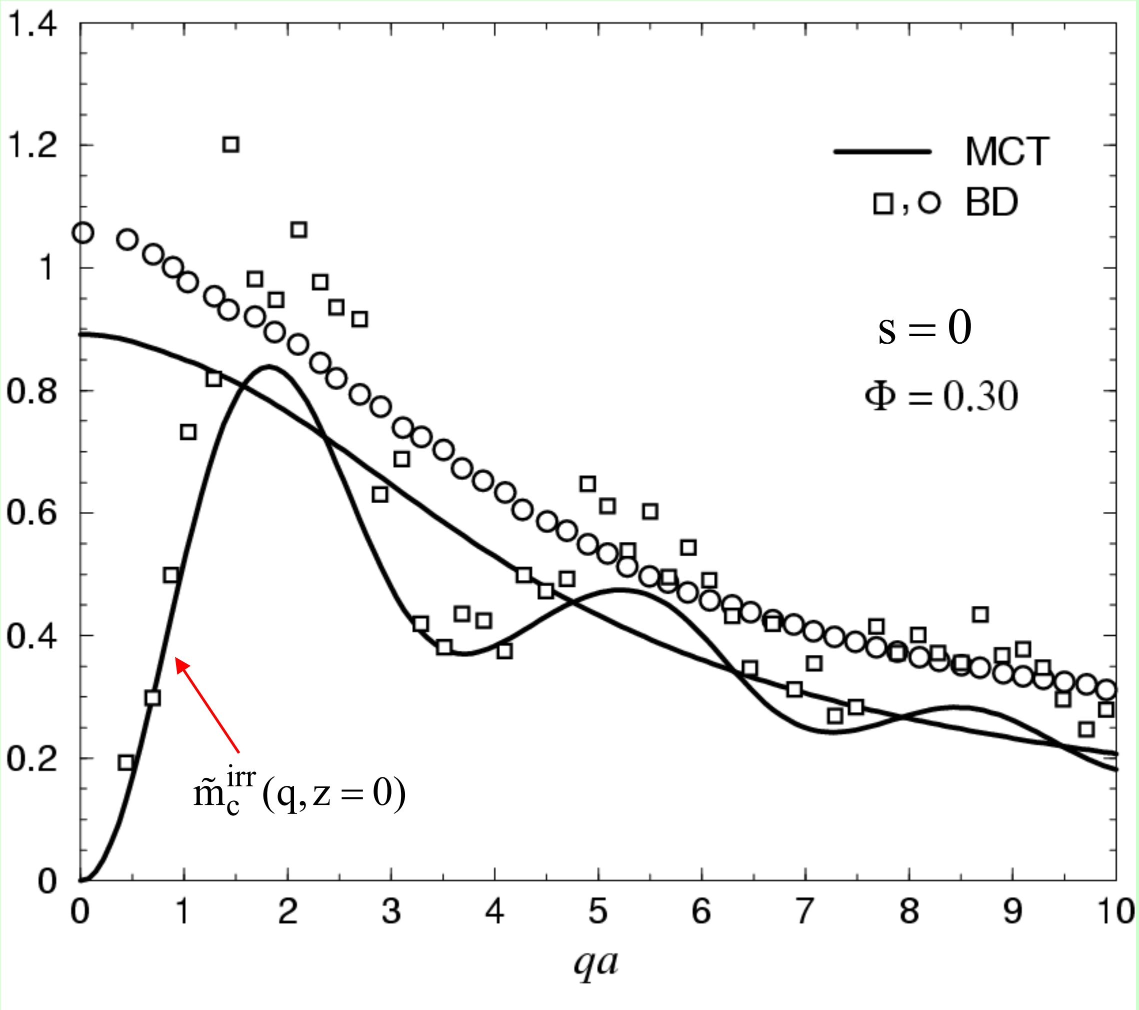
( Baur & Nägele, Physica A (1997))

- Measurable non-exponentiallity factor for charge-stabilized dispersion with $\sigma$ = 0.06



Theory: Banchio, Nägele & Bergenholtz, J. Chem. Phys. (2000)
Exp. + BD: Härtl et al., J. Chem. Phys. (1992)

- Time-integrated collective and self-dynamic irreducible memory functions

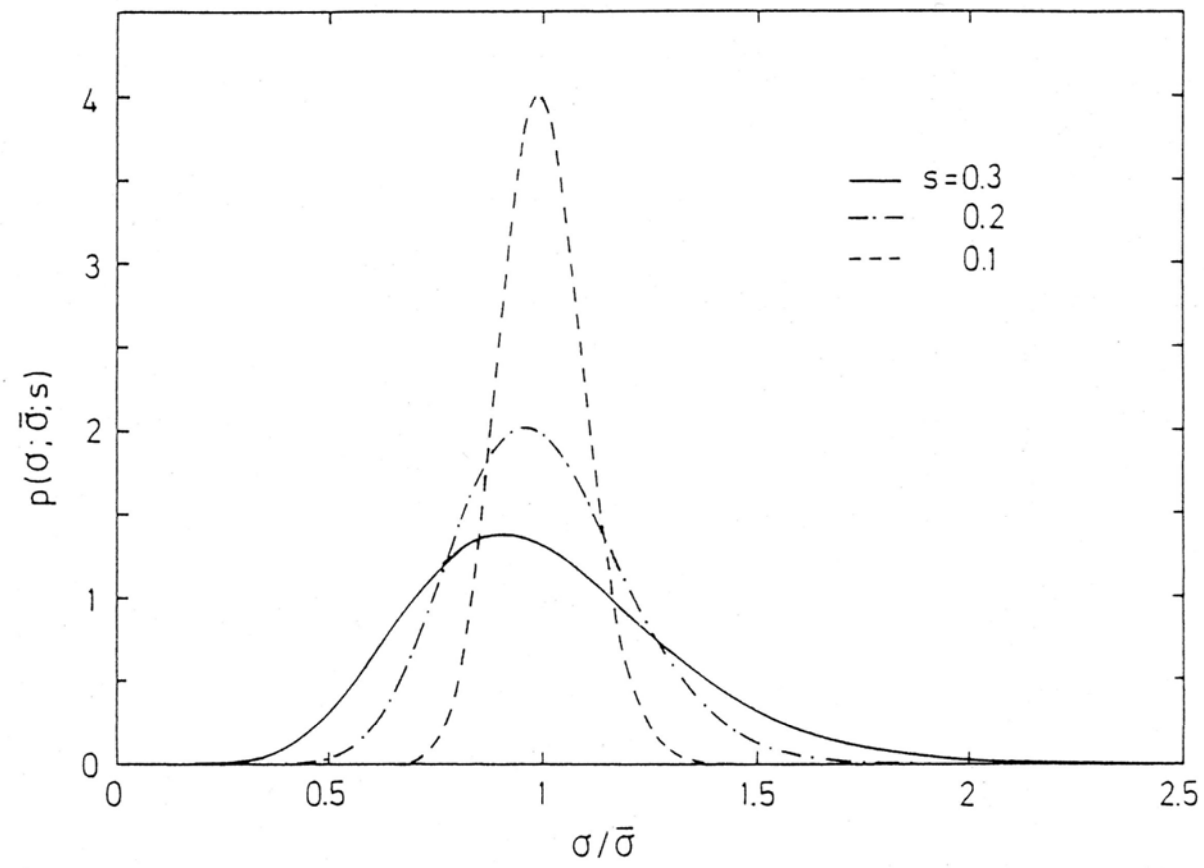


Hard spheres w/o HI

Theory: Banchio, Nägele & Bergenholtz, J. Chem. Phys. (2000)

Simulation: Cichocki & Hinsen, Ber. Bunsenges. Phys. Chem. (1990)

- Schultz distribution of particle sizes



# 9. Concluding remarks

- Colloidal dispersions: grand variety of dynamic properties
- Transport properties are determined by a delicate interplay of hydrodynamic and direct particle interactions
- Theoretical methods extendable to colloidal composites and polymer solutions
- There is an intensive & fruitful exchange between theory + experiment : quantitative theoretical predictions for colloidal model dispersions