# Rotational self-diffusion in suspensions of repulsive particles

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INNOVATIVE ECONOMY
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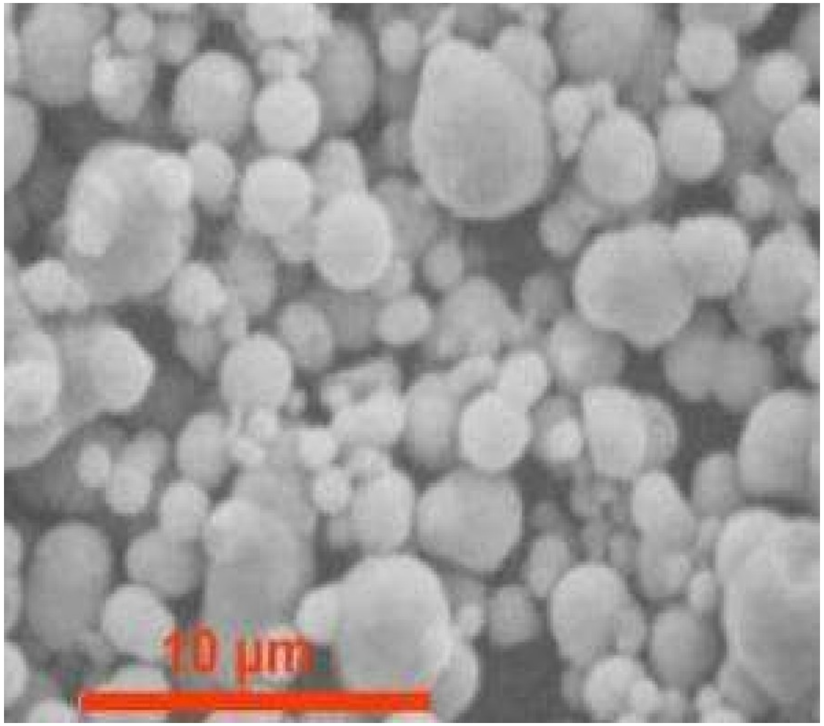
# Introduction - suspensions

*minute particles in liquid*

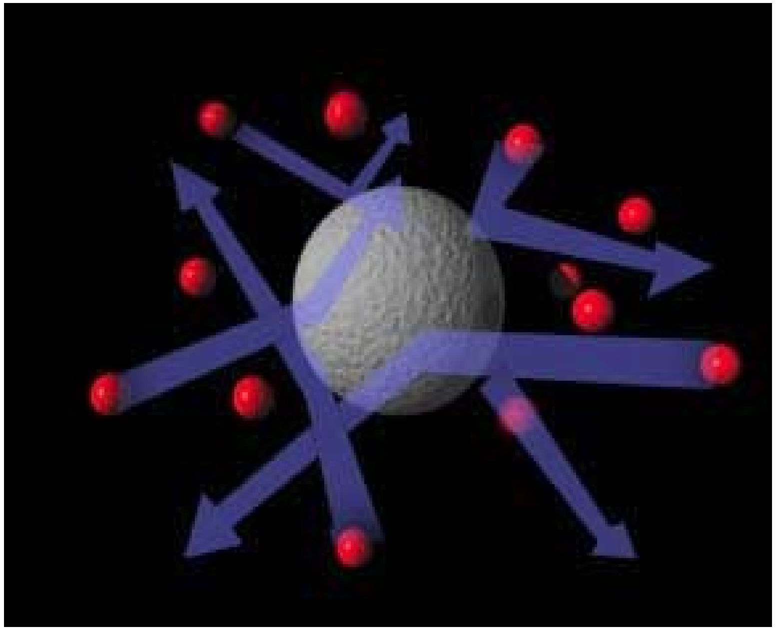



*Liquid:*
*-temperature* $T$
*-viscosity* $\mu$
*-density of the fluid* $\rho_f$

*Particles:*
*-radius* $a$
*-density of material* $\rho_p$
*-volume fraction* $\phi$

*milk, blood,...*
*magnetorheological fluid*

# Introduction – Brownian motion



$U$ - characteristic velocity (thermal)

$$Re = \frac{aU}{\nu}$$

*For Brownian translational diffusion of a fat globule in milk:*

$$a = 3\mu m, \quad T = 300K, \quad \nu = 8.9 \cdot 10^{-7} \frac{1}{sm^2} \quad \rho_f = 931 kg/m^3$$

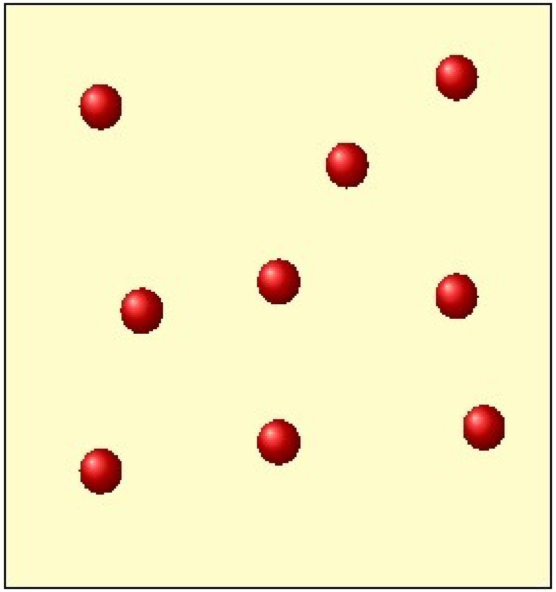
$$Re = 6.7 \cdot 10^{-4}$$

*For a=1nm would be* $Re = 0.037$

*Linearized Navier-Stokes equations*

# Hard-sphere suspension

*Unbounded liquid,*
*N particles*



*Stokes equations:*

$$\begin{aligned} \nabla p(\mathbf{r}) - \eta \Delta \mathbf{v}(\mathbf{r}) &= 0 \\ \nabla \cdot \mathbf{v}(\mathbf{r}) &= 0 \end{aligned}$$

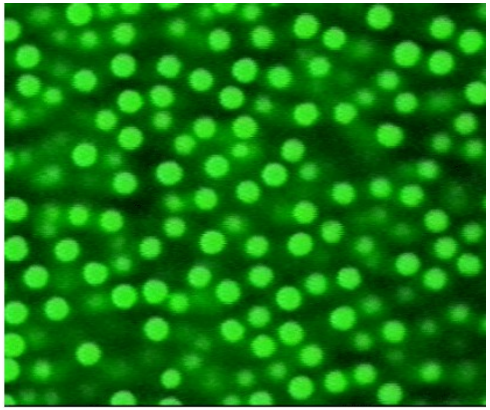
*Stick boundary conditions,*

$$\mathbf{v}(\mathbf{r}) \to \mathbf{v}_0(\mathbf{r}) \quad \textit{for} \quad r \to \infty$$

# Mobility matrix (when forces and torques are applied, quiescent fluid)

$$\begin{aligned} \mathbf{U}_i &= \sum_{j=1}^{N} \boldsymbol{\mu}_{ij}^{tt}(\mathbf{R}_1 \ldots \mathbf{R}_N) \cdot \mathbf{F}_j + \sum_{j=1}^{N} \boldsymbol{\mu}_{ij}^{tr}(\mathbf{R}_1 \ldots \mathbf{R}_N) \cdot \mathbf{T}_j \\ \boldsymbol{\Omega}_i &= \sum_{j=1}^{N} \boldsymbol{\mu}_{ij}^{rt}(\mathbf{R}_1 \ldots \mathbf{R}_N) \cdot \mathbf{F}_j + \sum_{j=1}^{N} \boldsymbol{\mu}_{ij}^{rr}(\mathbf{R}_1 \ldots \mathbf{R}_N) \cdot \mathbf{T}_j \end{aligned}$$

# Aim of our work



*Transport properties (short time):*
*-effective viscosity*
*-sedimentation coefficient*
*-diffusion coefficient*

To assess Beenakker-Mazur method in case of rotational self-diffusion coefficient for suspension of repulsive particles

$$D^r = \frac{k_B T}{3} \mathrm{Tr} \left[ \lim_{\infty} \left\langle \frac{1}{N} \sum_{i=1}^{N} \boldsymbol{\mu}_{ii}^{rr} \left( \mathbf{R}_1 \ldots \mathbf{R}_N \right) \right\rangle \right]$$

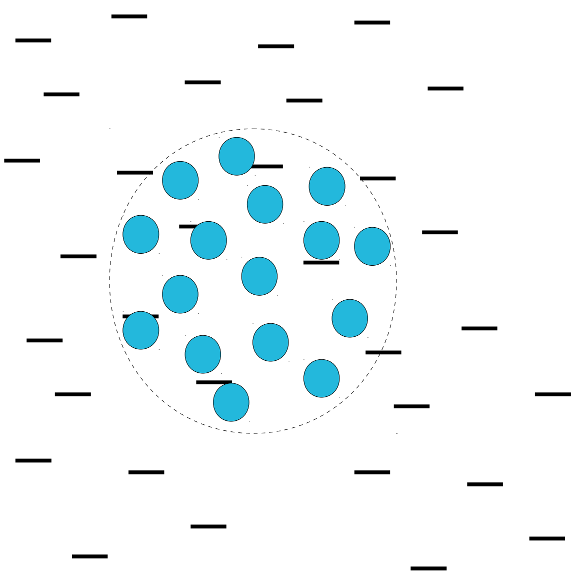
# Beginning of statistical physics considerations

*Einstein 1905 (corrected):*

$$\eta_{eff} = \eta(1 + \frac{5}{2}\phi)$$

$$D = \frac{k_B T}{6\pi\eta a}$$

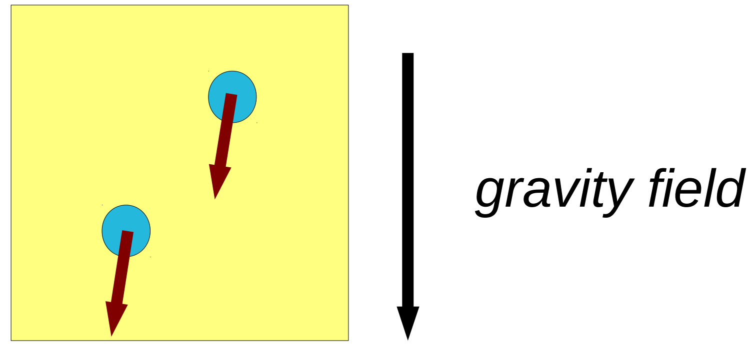
$$\phi = \frac{4}{3}\pi a^3 n$$

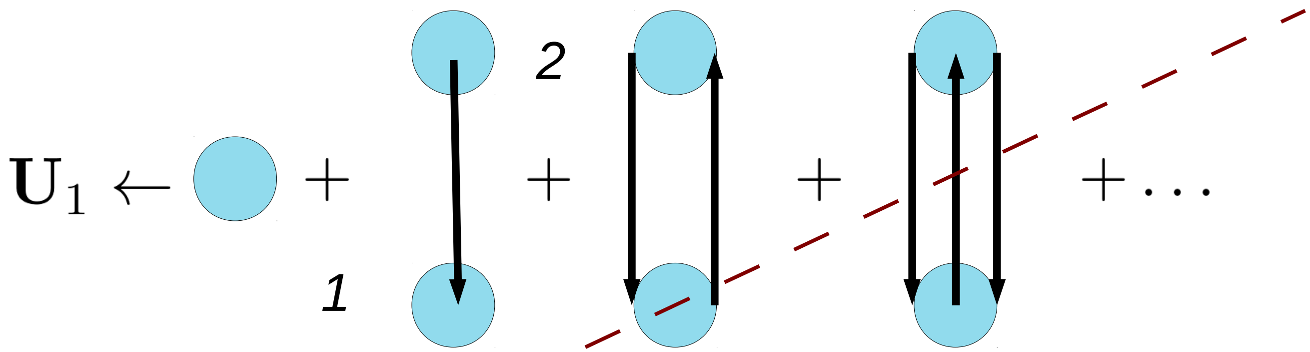


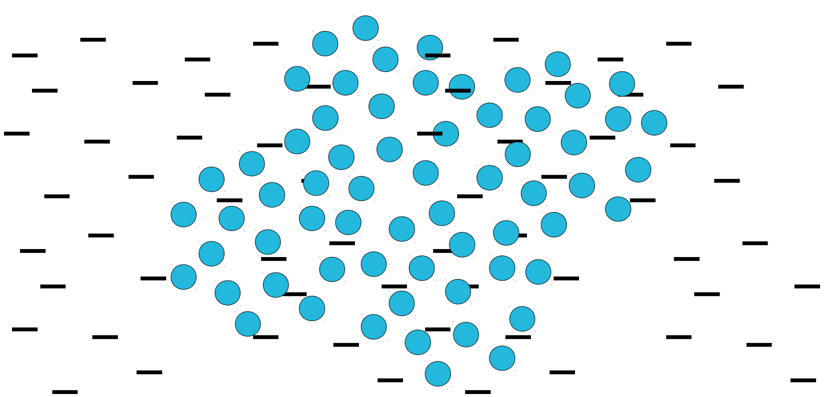
*ambient (shear) flow* $\mathbf{v}_0(\mathbf{r})$

- *Finite system*
- *Hydrodynamic interactions neglected (no reflections, single particle)*

# *Hydrodynamic interactions – Smoluchowski (1911)*



$$\int d^3r \left|\mathbf{G}(\mathbf{r})\right| = \infty$$

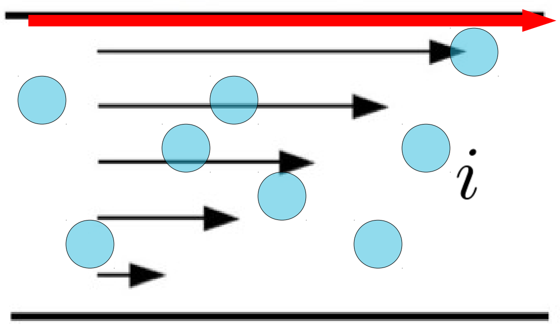
$$\mathbf{G}(\mathbf{r}) = \frac{1}{8\pi\eta}\frac{\mathbf{1} + \hat{\mathbf{r}}\hat{\mathbf{r}}}{r}$$

*Well defined expression for effective viscosity?*

# *Beyond diluted suspensions*

*Saito (1950):*

*-extension of Einstein work on mean-field level*

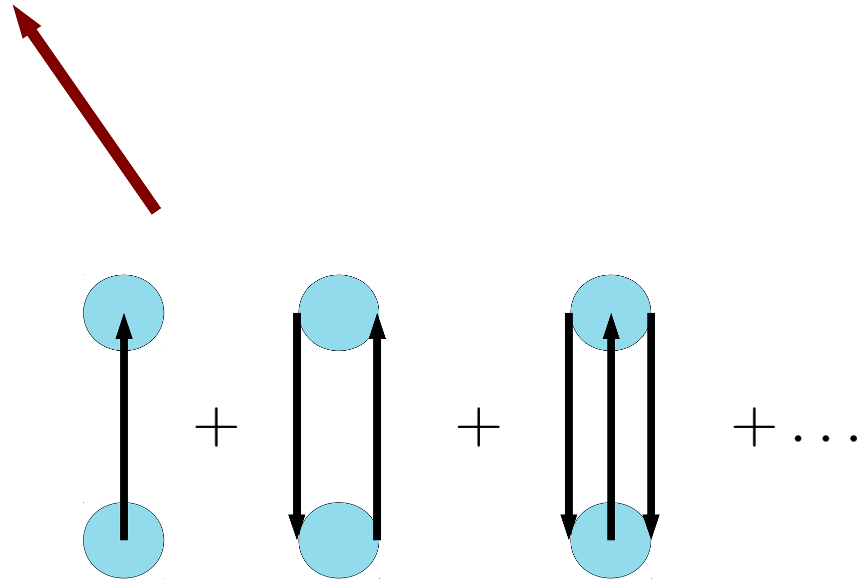


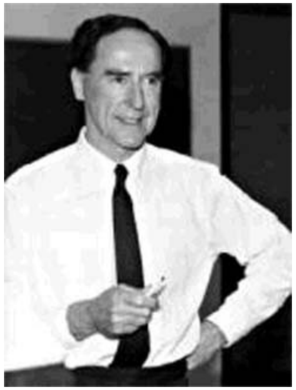

$$\frac{\eta_{eff}}{\eta} = \frac{1 + \frac{3}{2}\phi}{1 - \phi}$$

*non-absolutely convergent integrals!*

# Two-particle hydrodynamic interactions (1972)

$$\frac{\eta_{eff}}{\eta} = 1 + \frac{5}{2}\phi + a_2\phi^2 + \ldots$$





*absolute convergence*

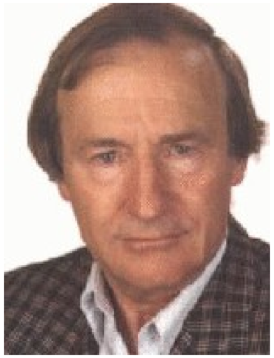
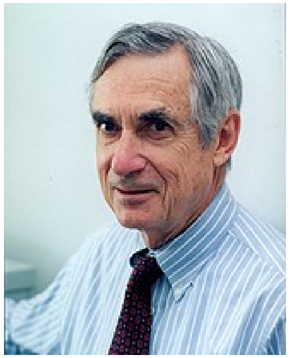
*Batchelor, Green (1972):* $a_2 \approx 5.2$

$$\int d^3r \left|\mathbf{G}(\mathbf{r})\right| = \infty$$

*(ad hoc renormalization)*

*Problem with long-range HI still not solved*

# 1982 – problem of long-range HI solved


**B. U. Felderhof,[1] G. W. Ford,[2] and E. G. D. Cohen[3]**

*Received August 24, 1981*

We derive a cluster expansion for the electric susceptibility kernel of a dielectric suspension of spherically symmetric inclusions in a uniform background. This also leads to a cluster expansion for the effective dielectric constant. It is shown that the cluster integrals of any order are absolutely convergent, so that the dielectric constant is well defined and independent of the shape of the sample in the limit of a large system. We compare with virial expansions derived earlier in

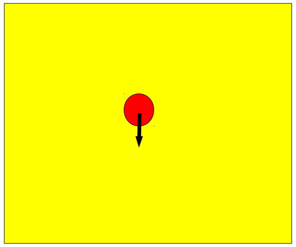
*dielectric <=> suspension*

# *Hydrodynamic interactions*

## *Many-body character*

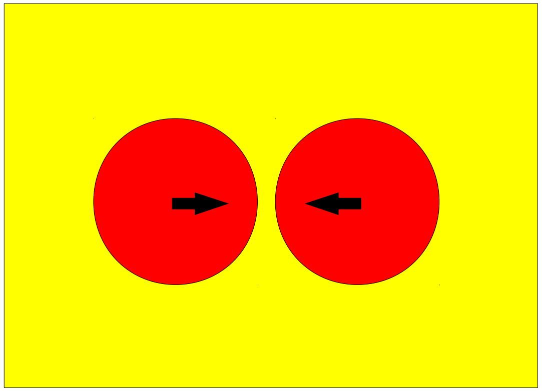
*two-body approximation relevant for volume fractions less than about 5%*

## *Long-range character*



$$\mathbf{v}(\mathbf{r}) \sim \mathbf{G}(\mathbf{r}) \cdot \mathbf{F}$$

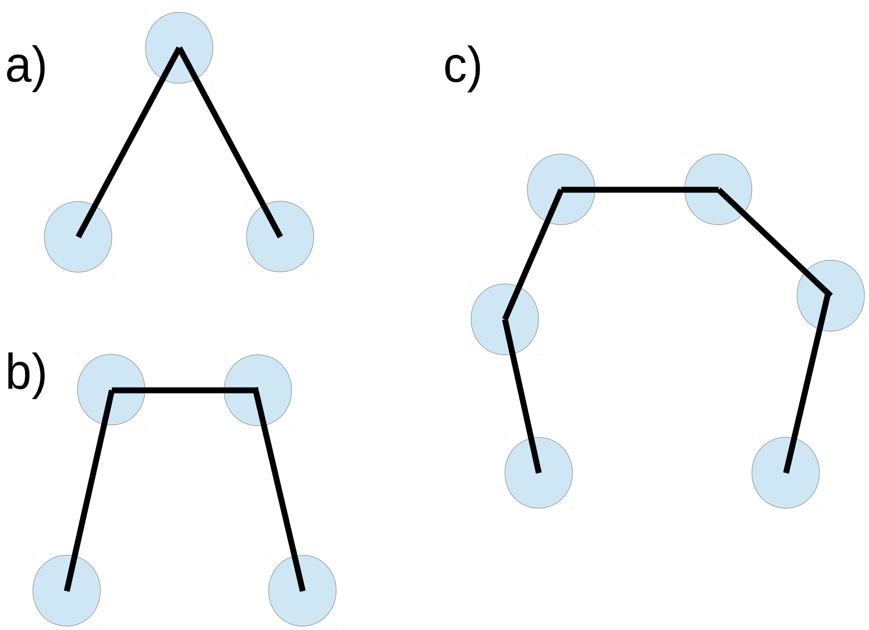
## *Strong interactions of close particles*

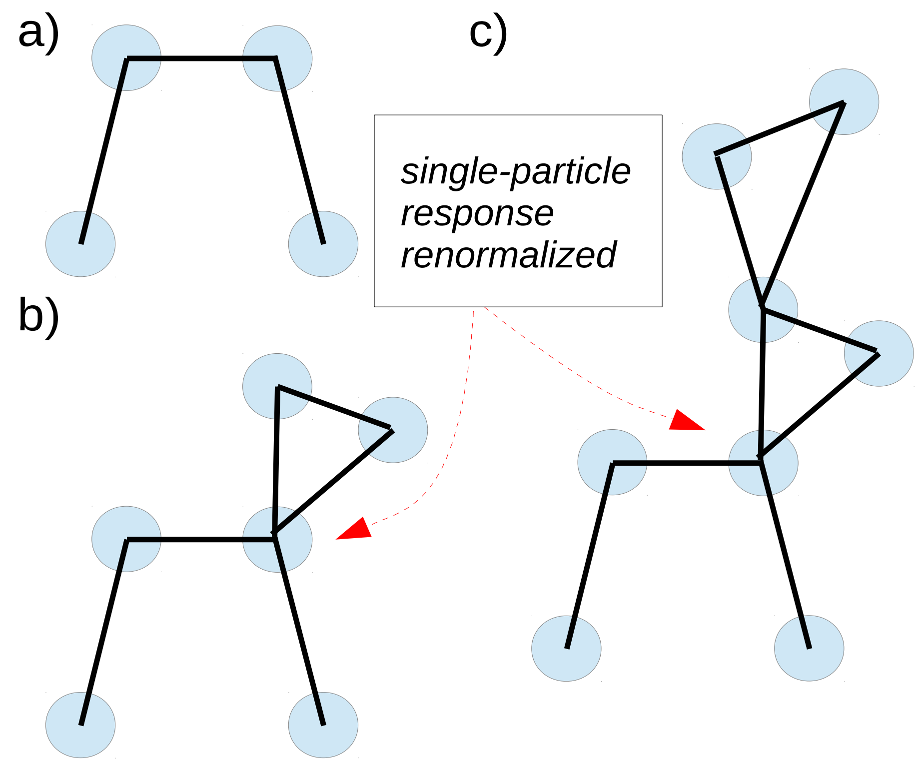


*For constant velocities*
*asymptotically infinite drag force*
*(Jeffrey, Onishi (1984))*

# *Beenakker-Mazur method (1983)*

Idea of the method – resummation of certain class of hydrodynamic interactions – 'ring-selfcorrelations'




No correlations in position between particles in the above resummed terms

# Beenakker-Mazur method (1983)

*Ring-selfcorrelations:*

$$G^s_{\langle \mathcal{M}_R \rangle}(\mathbf{R},\mathbf{R}') = \begin{cases} G_{\langle \mathcal{M}_R \rangle}(\mathbf{R},\mathbf{R}') & \text{for } \mathbf{R} = \mathbf{R}' \\ 0 & \text{for } \mathbf{R} \neq \mathbf{R}' \end{cases}$$

$$\mathcal{M}_R = \mathcal{M}\left(1 - G^s_{\langle \mathcal{M}_R \rangle}\mathcal{M}\right)^{-1}$$

$$G_{\langle \mathcal{M}_R \rangle} = \tilde{G}\left(1 - \langle \mathcal{M}_R \rangle \tilde{G}\right)^{-1}$$

# Beenakker-Mazur method (1983)

$$\mathcal{T} = \mathcal{M} + \mathcal{M} G_{\langle \mathcal{M}_R \rangle} \left[ 1 - \left( \mathcal{M}_R - \langle \mathcal{M}_R \rangle \right) \tilde{G}_{\langle \mathcal{M}_R \rangle} \right]^{-1} \mathcal{M}_R$$

*kernel of "mobility matrix"*

*renormalized fluctuations expansion*

*Beenakker-Mazur: the above expression up to second order*
*=> also called delta gamma scheme*

# Beenakker and Mazur scheme

*Beenakker and Mazur scheme – expansion in density fluctuations (1983). The most comprehensive statistical physics theory for short times properties of suspension nowadays*

- ✓ *Many-body character*
- ✓ *Long-range character*
- ✗ *Strong interactions of close particles*

*No satisfactory statistical physics method including the above three features*

*Lubrication important!*

*Propagator does not depend  on correlations (rdf)* $G_{\langle \mathcal{M}_R \rangle}$

*How interactions (e.g. electrostatic) influence results of Beenakker-Mazur method?*

*Check for rotational self-diffusion coefficient...*

# Treloar, Masters (1989)

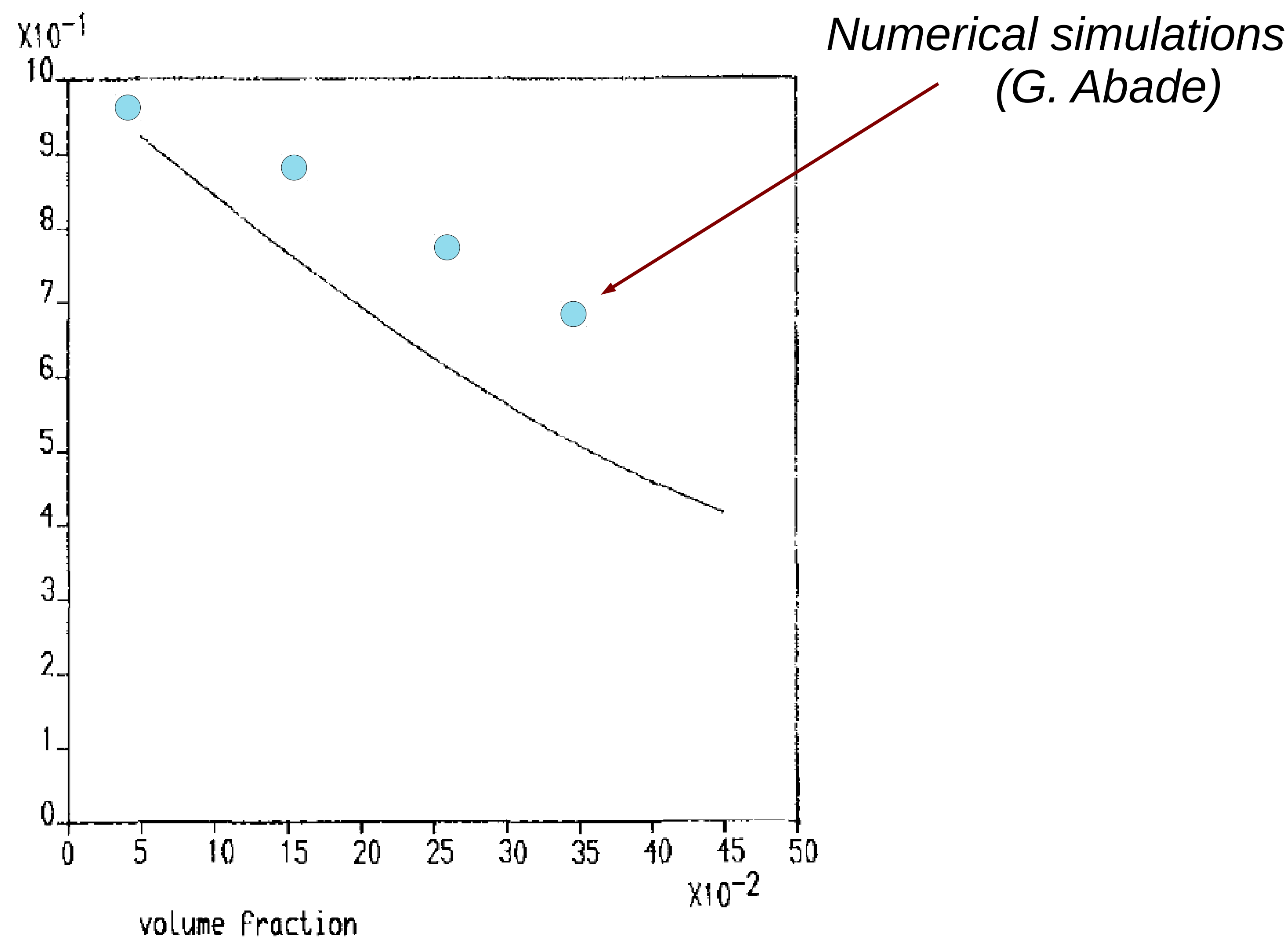


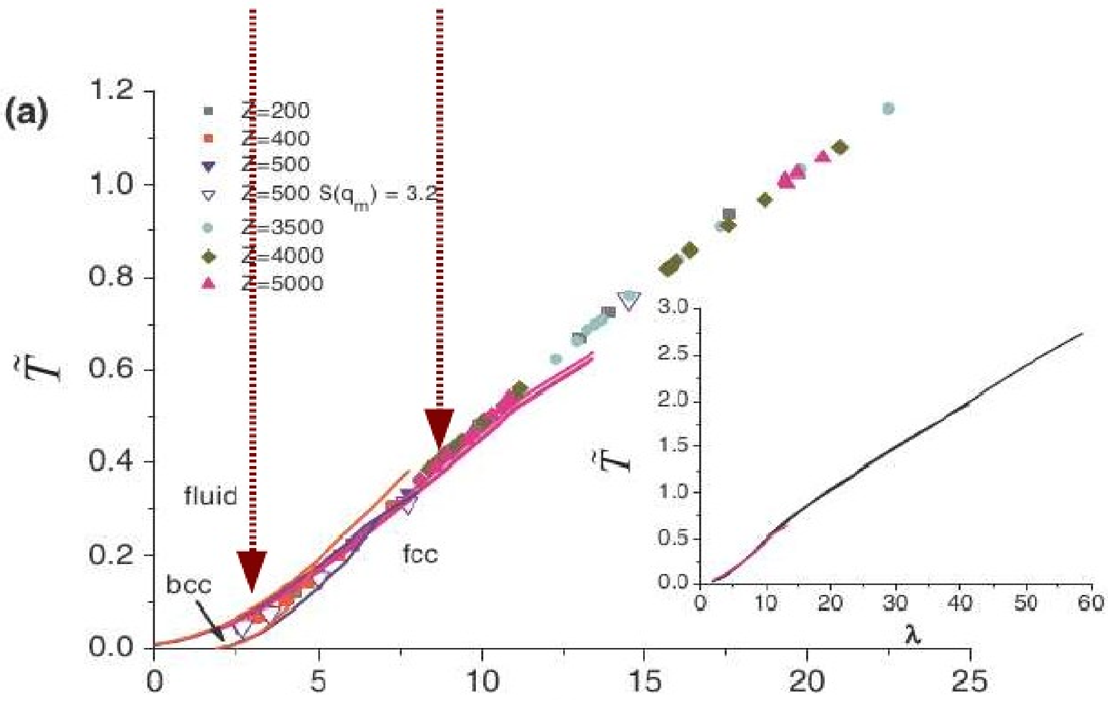

Figure 1. A plot of the normalized single particle rotational mobility, $\mu_S^{RR}/\mu_0^{RR}$, calculated to second order in the $\delta\gamma$-expansion, against volume fraction, $\phi$.

# Yukawa-hard core repulsive potential

*screening length*

$$\frac{u(r)}{k_B T} = \begin{cases} \frac{1}{\tilde{T}} e^{\lambda} e^{-\lambda r/\langle r \rangle} \frac{\langle r \rangle}{r} & \text{for } r > 2a \\ \infty & r < 2a \end{cases}$$

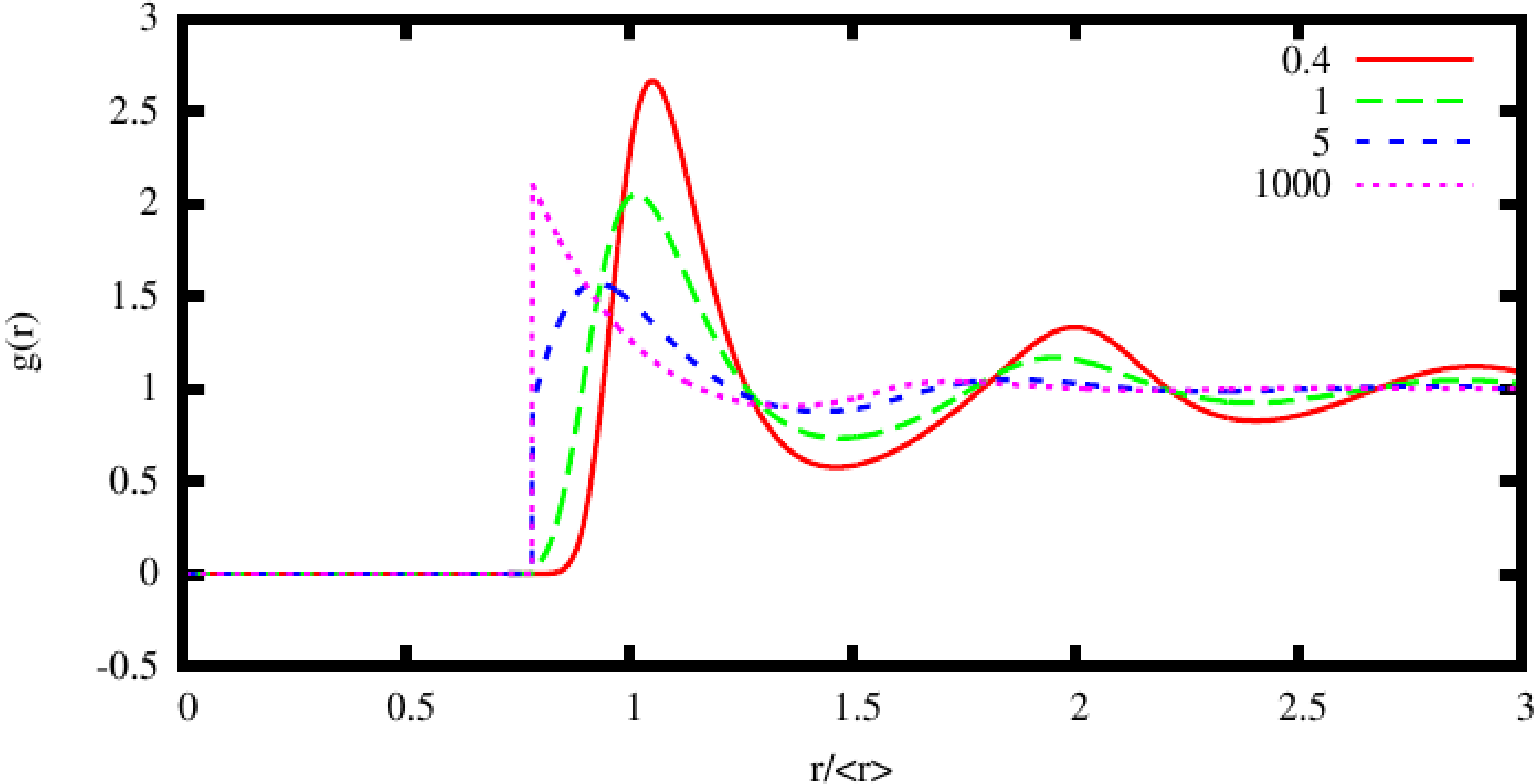
*For constant* $\lambda$ *, the limit of hard sphere is for* $\tilde{T} \to \infty$



# *Radial distribution function*

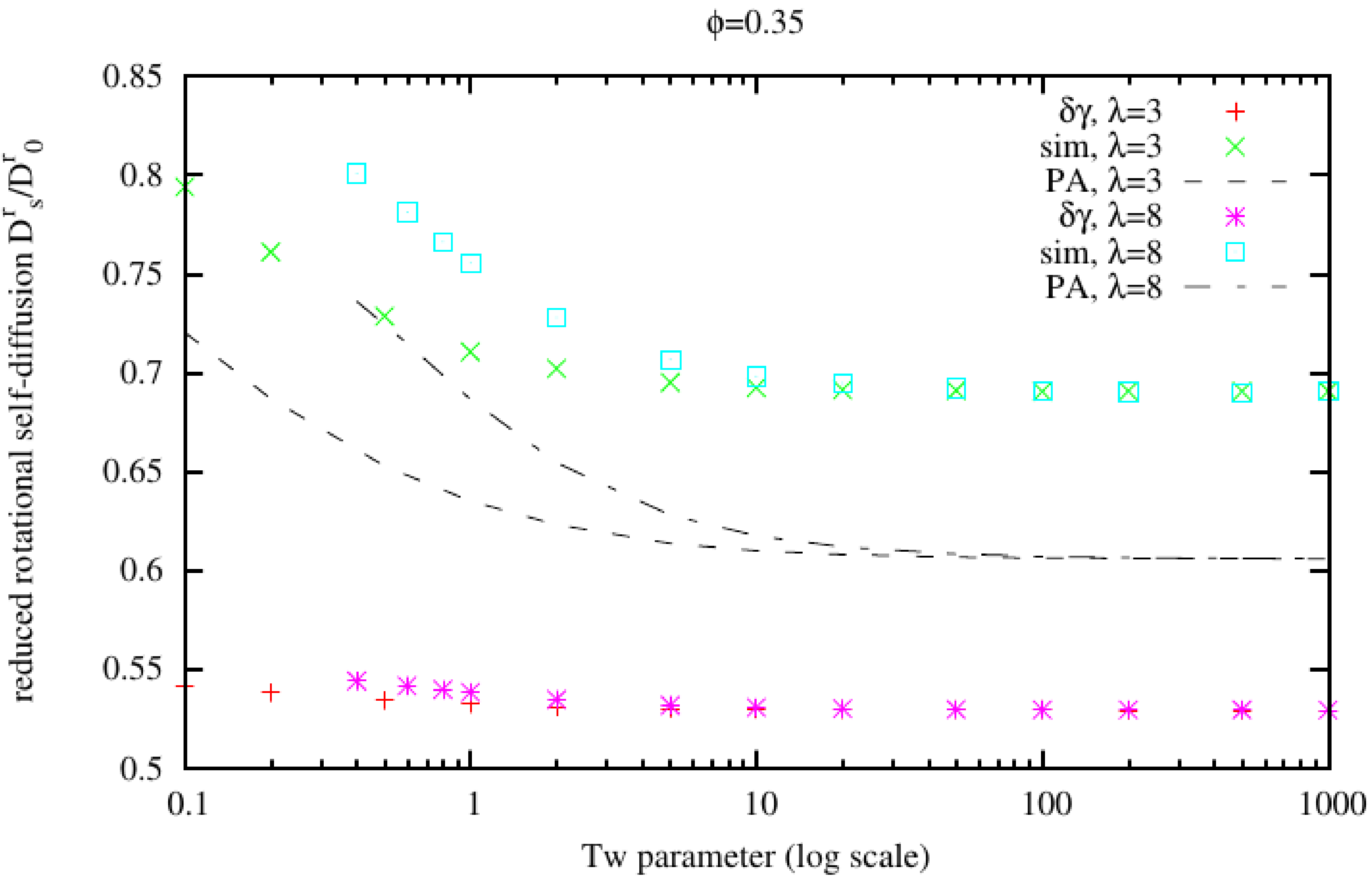
Radial distribution function calculated by Rogers-Young scheme
(results similar to Monte Carlo calculations)

Repulsion decreases number of close pairs in the system




$$\phi = 0.25 \quad \lambda = 8 \quad \tilde{T} = 0.4, 1, 5, 1000$$

# Rotational self-diffusion coefficient for repulsive particles by Beenakker-Mazur method



# Summary

- Assessment of Beenakker-Mazur method - by rotational self-diffusion coefficient calculated for repulsive particles
- Two-body hydrodynamic interactions better than BM method
- Weak dependence of BM on structure of suspension on rotational self-diffusion

*Ongoing research in colaboration with:*

*Gerhard Nägele*
*Research Centre Jülich*

*Gustavo Abade*
*Universität Konstanz*

*Marco Heinen*
*Caltech*

*Important contribution: Eligiusz Wajnryb, IPPT*

# *Surface forces for freely moving particles in ambient flow* $\mathbf{v}_0(\vec{r})$

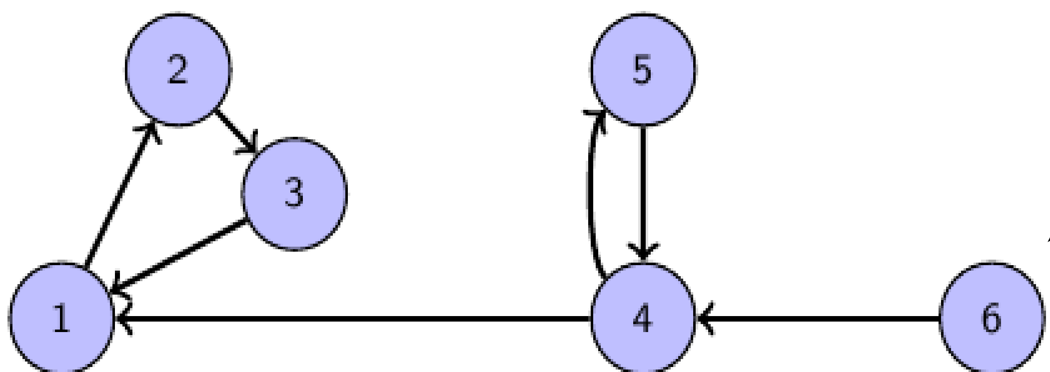
*forces on surface of particle i:* $$\mathbf{f}_i(\mathbf{r}) \leftarrow \mathbf{v}_0(\mathbf{r})$$

*When Stokes equations solved by method of reflections (Smoluchowski 1911):*

$M(6) : \mathbf{v}(\mathbf{r}) \longrightarrow \mathbf{f}_6(\mathbf{r})$

*single particle, (Felderhof 1976)*

$\mathbf{f}_1(\mathbf{r}) \ni$




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

*scattering sequence*

$$M(1)GM(3)GM(2)GM(1) \times$$
$$G \times M(4)GM(5)GM(4) \times G \times M(6)$$

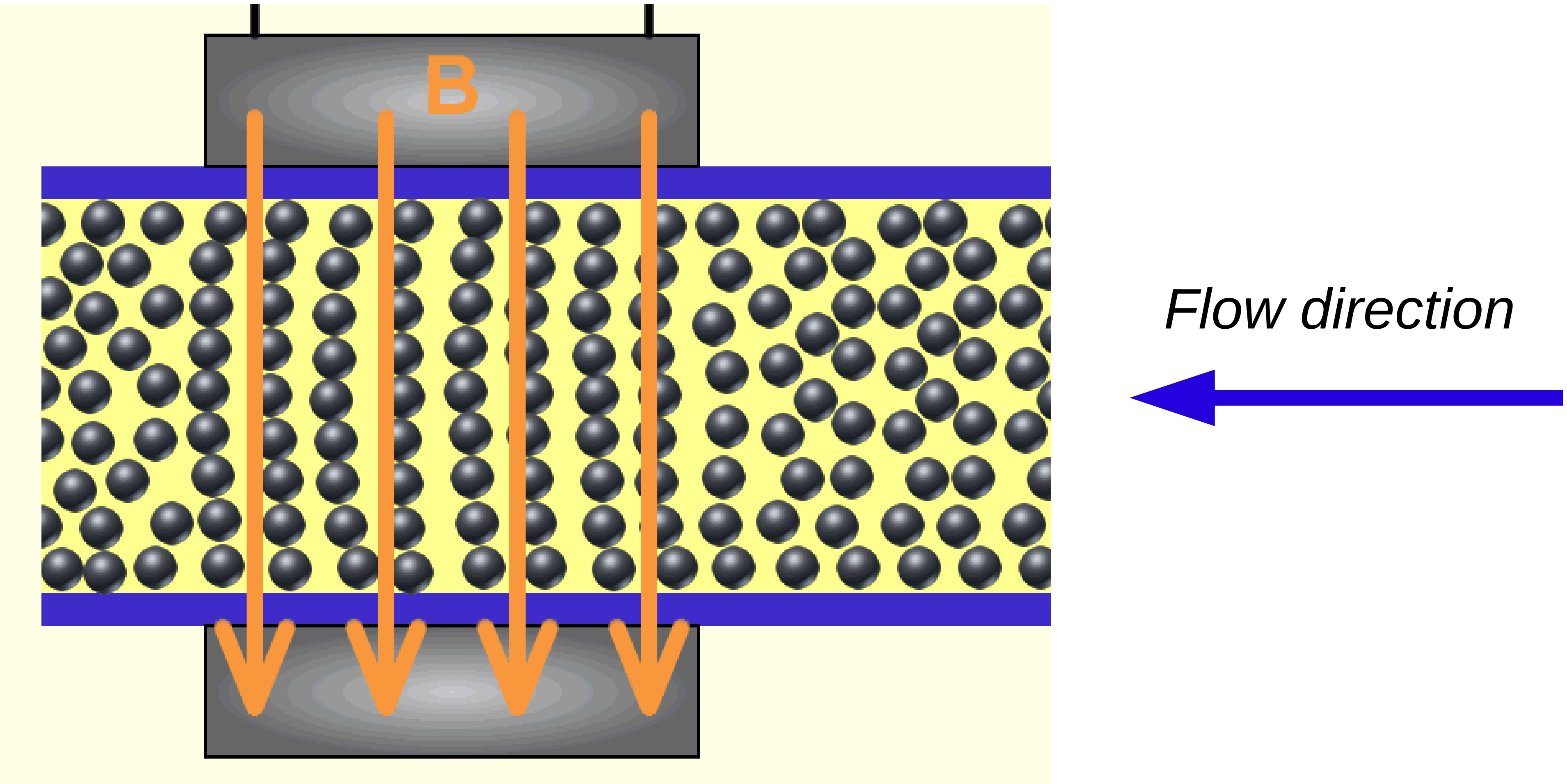
*scattering series*

*Oseen tensor (Green function for Stokes eqs):*

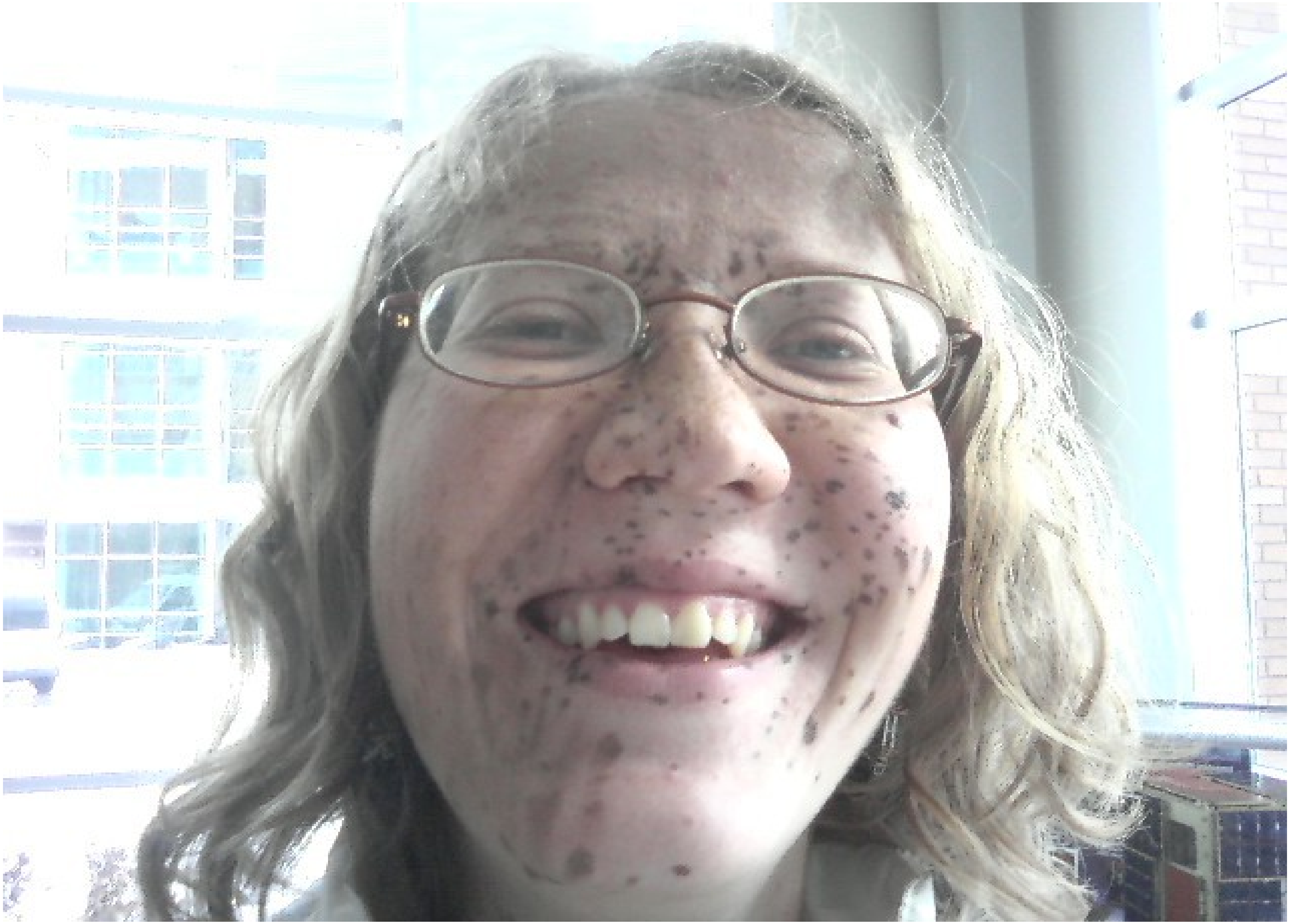
$$G(\mathbf{r}) = \frac{1}{8\pi\eta} \frac{\mathbf{1} + \hat{\mathbf{r}}\hat{\mathbf{r}}}{r}$$

*Probability distribution for position of particles:* $$p(1 \ldots N)$$

# *Introduction – different phenomena*




Magnetic field modifies velocity flow under constant pressure gradient (qualitative understanding sometimes easy)



*“... ferrofluid explosion on me ...”*