Transport properties of colloidal suspensions

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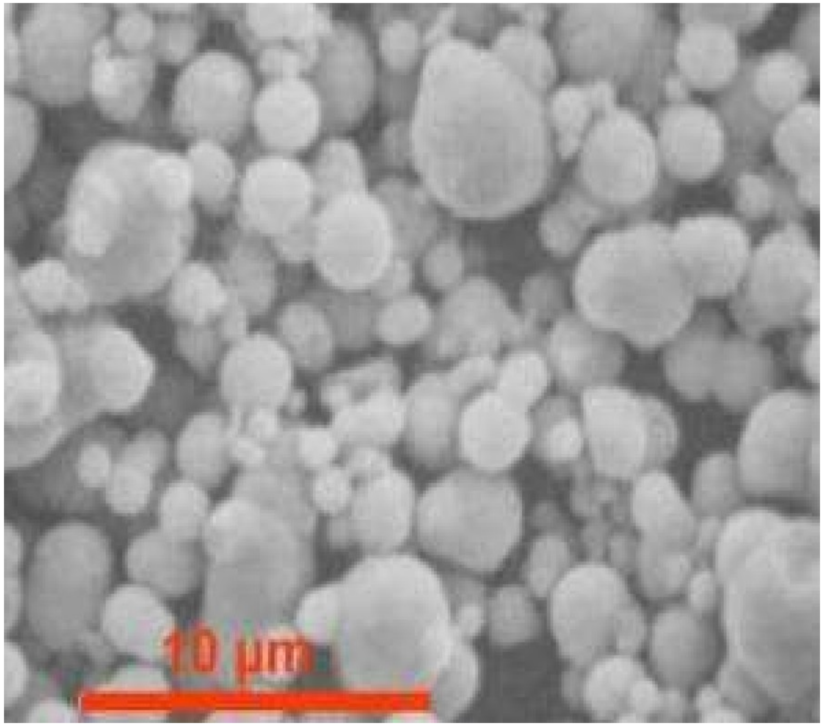
Introduction - suspensions

minute particles in liquid



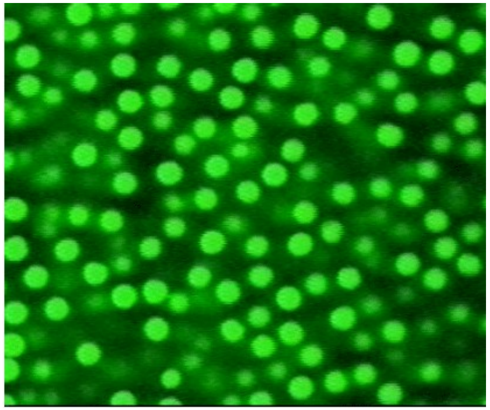
Liquid:
-temperature T
-viscosity μ
-density of the fluid ρ_f

Particles:
-radius a
-density of material ρ_p
-volume fraction ϕ

milk, blood,...

Goal of our work

Monodisperse suspension
of spherical particles

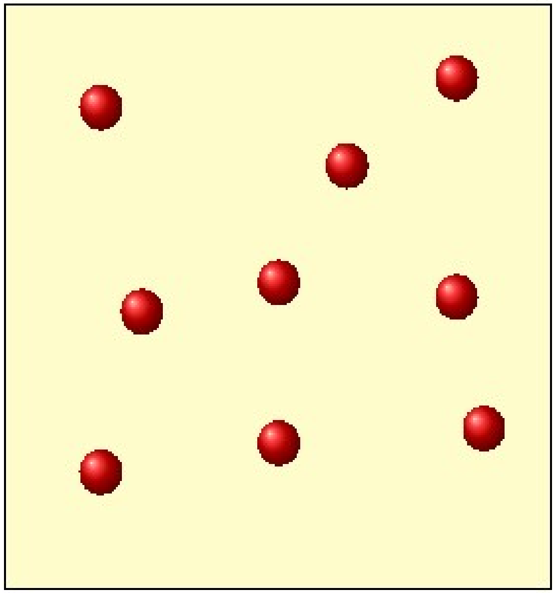


Transport properties (short time):
-effective viscosity
-sedimentation coefficient
-diffusion coefficient

Over 100 years of research - still an open question

Hard-sphere suspension

Unbounded liquid,
N particles in configuration $X \equiv \mathbf{R}_1, \ldots, \mathbf{R}_N$



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,

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

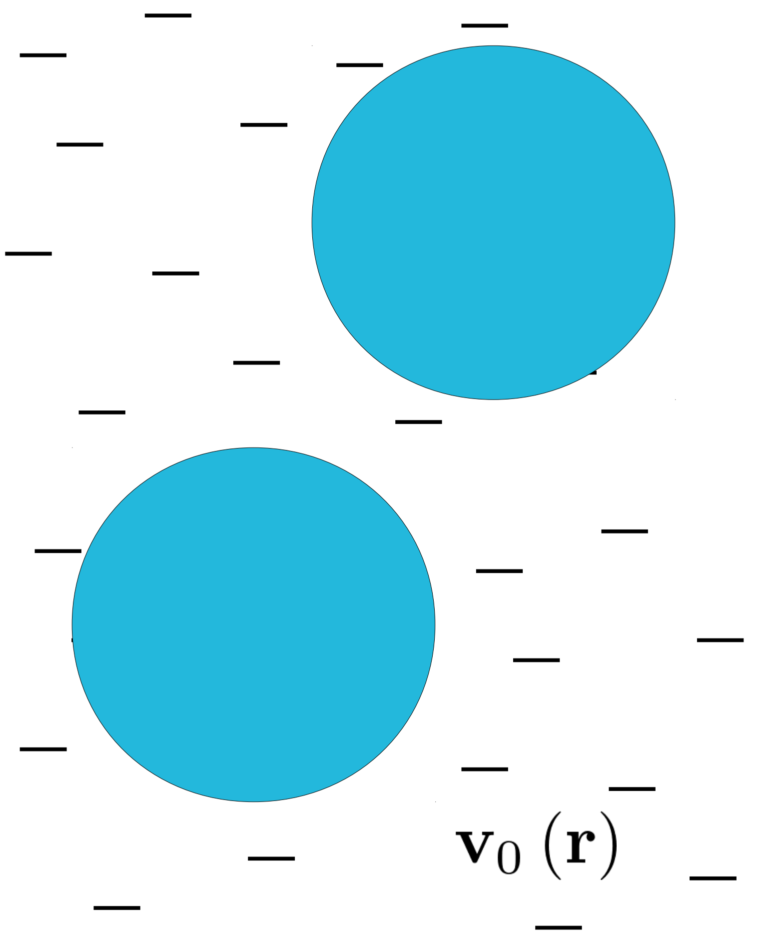
Effective viscosity

Landau: effective viscosity related to force on the surface of particles

$$\mathbf{f}_i(\mathbf{r}) = -\sigma(\mathbf{r}; X)\hat{\mathbf{n}}(\mathbf{r})\delta(|\mathbf{r} - \mathbf{R}_i| - a)$$

stress tensor

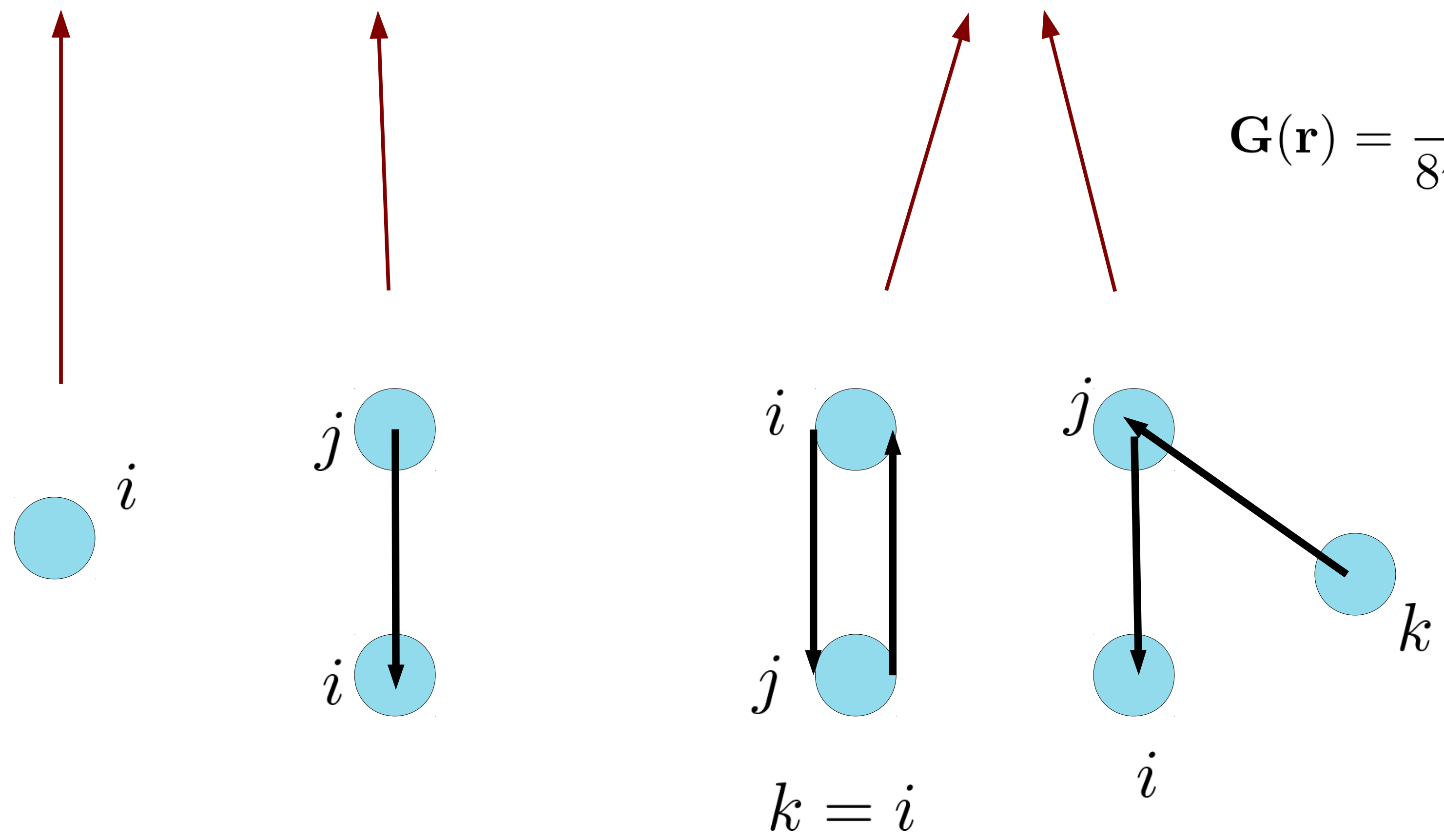
vector normal to the surface of particle i



Scattering series

$$\mathbf{f}_i = \left(\mathbf{M}(i) + \sum_{j \neq i} \mathbf{M}(i)\mathbf{G}\mathbf{M}(j) + \sum_{j \neq i} \sum_{k \neq j} \mathbf{M}(i)\mathbf{G}\mathbf{M}(j)\mathbf{G}\mathbf{M}(k) + \ldots \right) \mathbf{v}_0$$

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



suspension <=> dielectrics <=> other systems

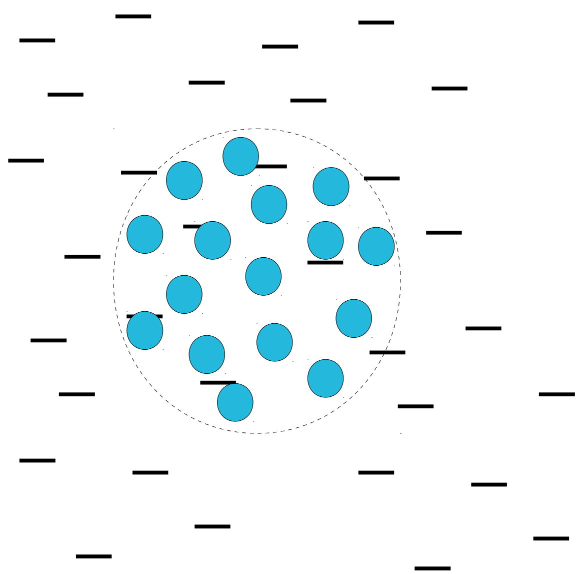
Transport properties – history and scattering series

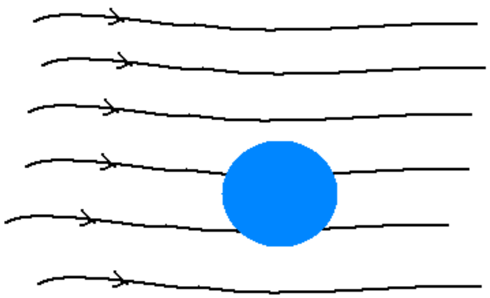
Einstein 1905
(corrected):

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

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

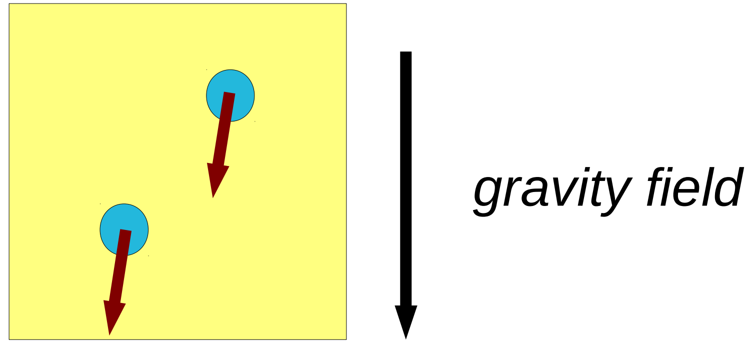
Single particle in ambient (shear) flow $\mathbf{v}_0(\mathbf{r})$

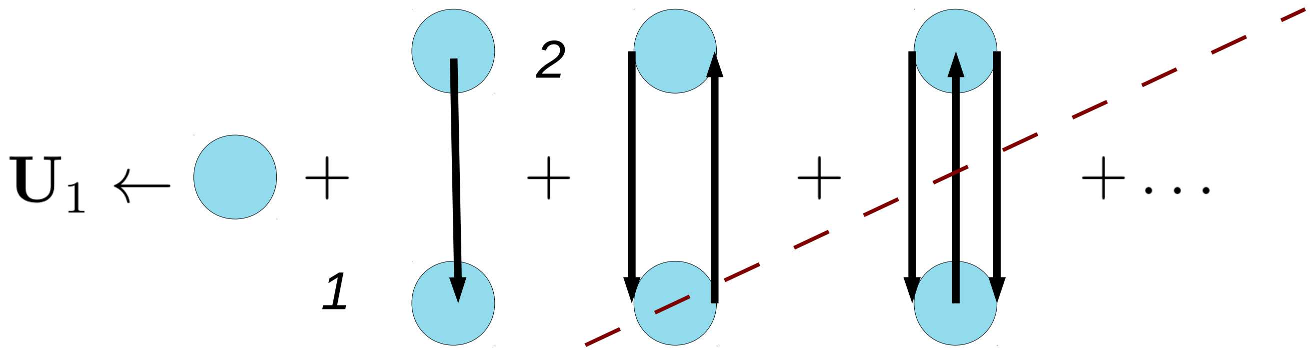


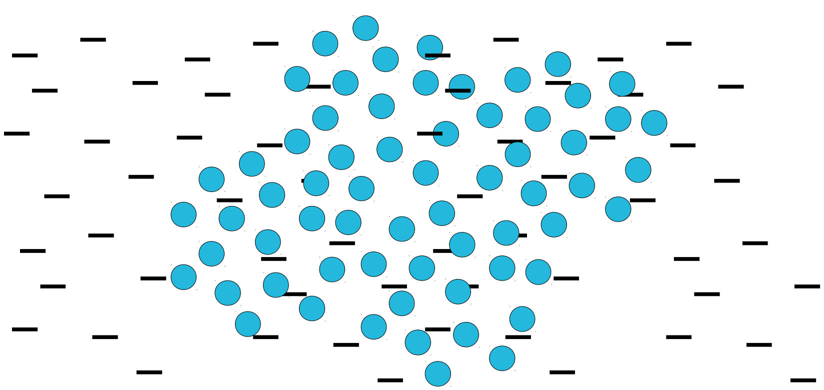


- *Finite system*
- *Hydrodynamic interactions neglected*
  (no reflections, single particle)

Hydrodynamic interactions – Smoluchowski (1911)







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

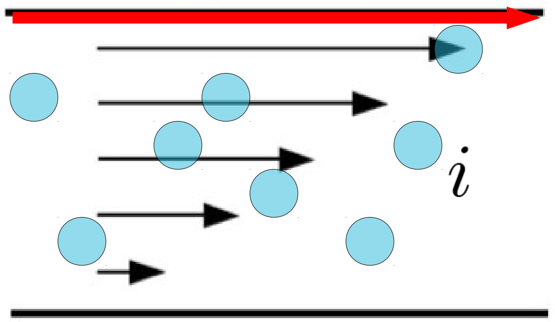
$$\mathbf{G}(\mathbf{r}) = \frac{1}{8\pi\eta}\,\frac{\mathbf{1}+\hat{\mathbf{r}}\hat{\mathbf{r}}}{r}$$

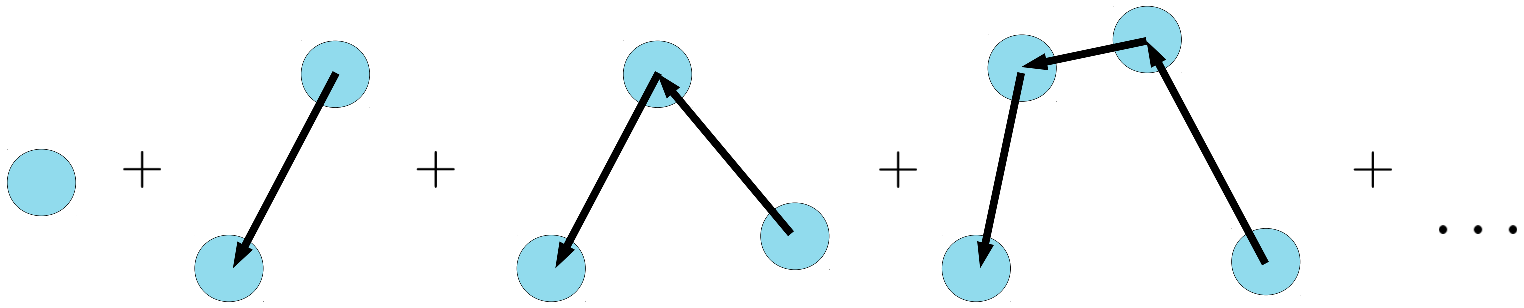
Well defined expression for effective viscosity?

Beyond diluted suspensions

Saito (1950):

-extension of Einstein work on mean-field level





$$\mathbf{M}(\mathbf{R}_i)\mathbf{G}\mathbf{M}(\mathbf{R}_j) \to W(\mathbf{R}_i - \mathbf{R}_j)\mathbf{M}(\mathbf{R}_i)\mathbf{G}\mathbf{M}(\mathbf{R}_j)$$

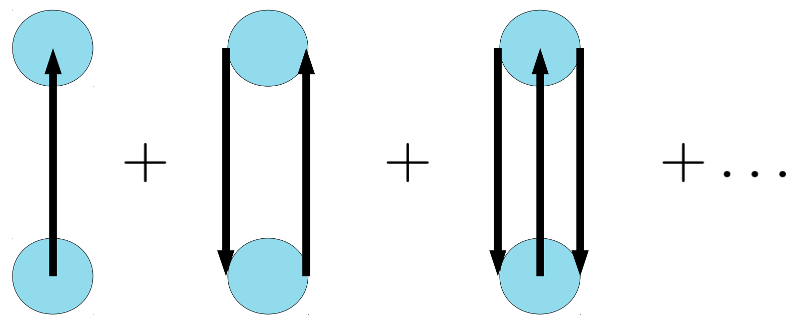
vanishes when two particles overlap

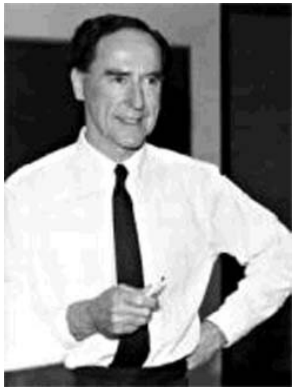
$$\frac{\eta_{eff}}{\eta} = \frac{1+\frac{3}{2}\phi}{1-\phi}$$

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)

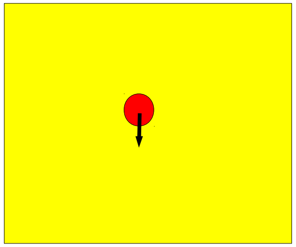
Problem with long-range HI still not solved

Hydrodynamic interactions

Many-body character

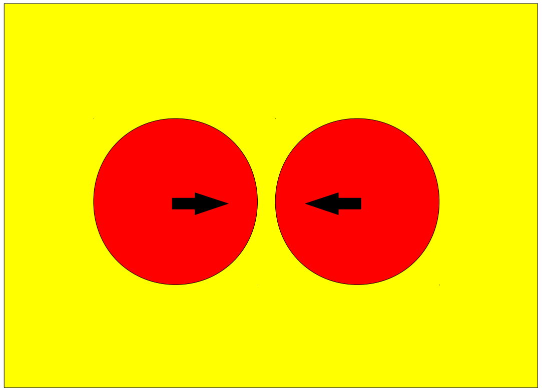
two-body approximation relevant for volume fractions less than about 5%

Long-range character



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

Strong interactions of close particles



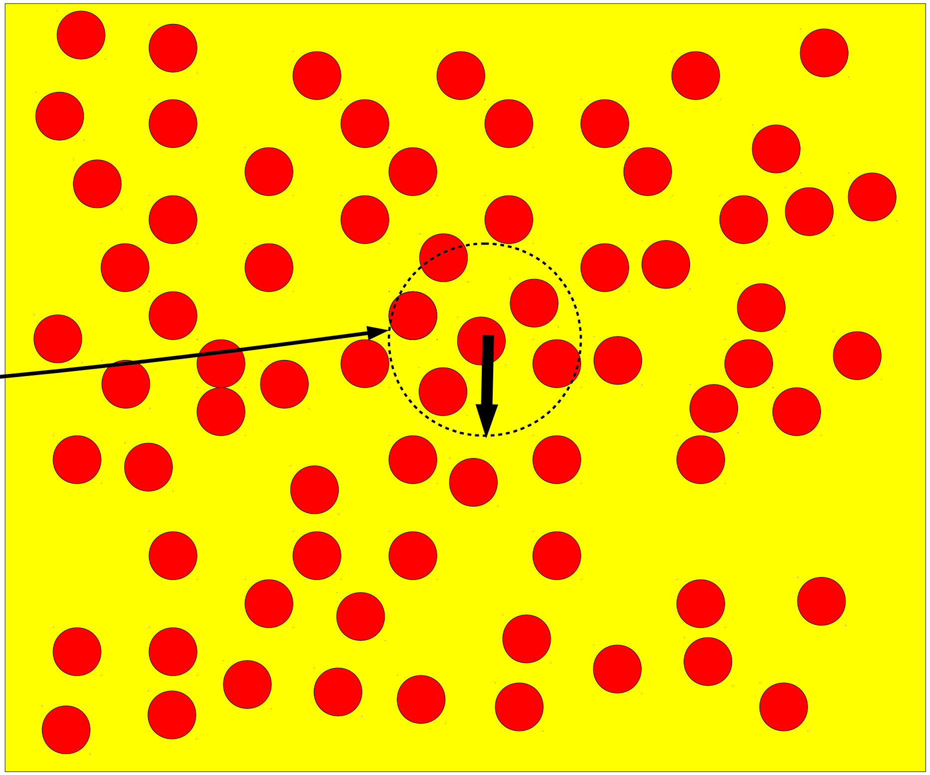
For constant velocities asymptotically infinite drag force (Jeffrey, Onishi (1984))

Effective Green function
– includes all three features of hydrodynamic interactions

Flow caused by force acting on particles in the area

total force acting on particles in the area

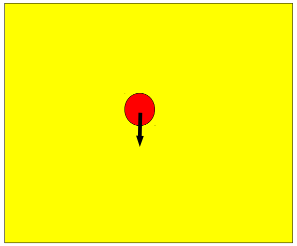
$$\mathbf{v}\left(\mathbf{r}\right) \sim \mathbf{G}_{\mathrm{eff}}\left(\mathbf{r}\right)\mathbf{F}$$



effective Green function
(effective propagator):

$$\mathbf{G}_{\mathrm{eff}}(\mathbf{r}) \sim \frac{1}{8\pi\eta_{\mathrm{eff}}}\frac{\mathbf{1}+\hat{\mathbf{r}}\hat{\mathbf{r}}}{r} = \frac{\eta}{\eta_{\mathrm{eff}}}\mathbf{G}(\mathbf{r})$$

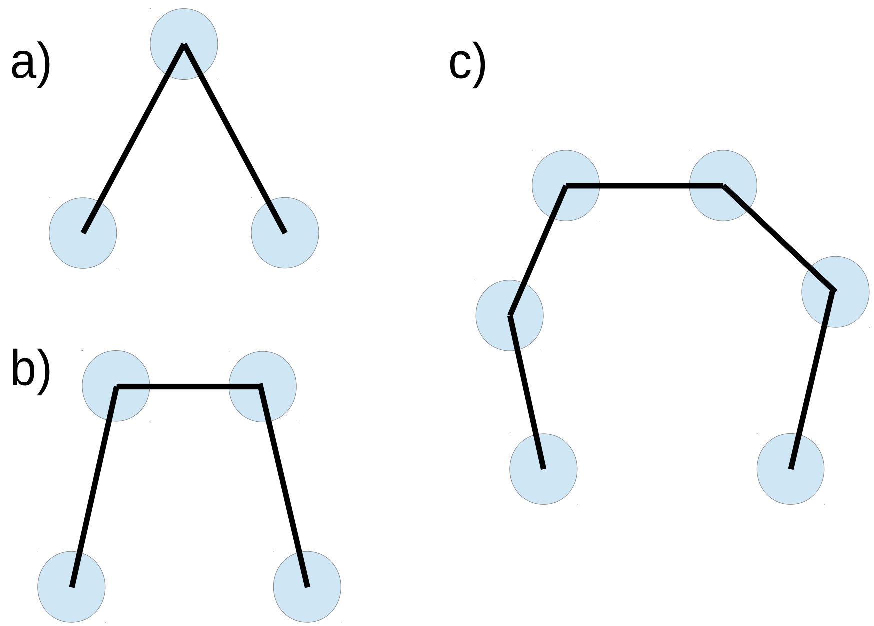
at the distance

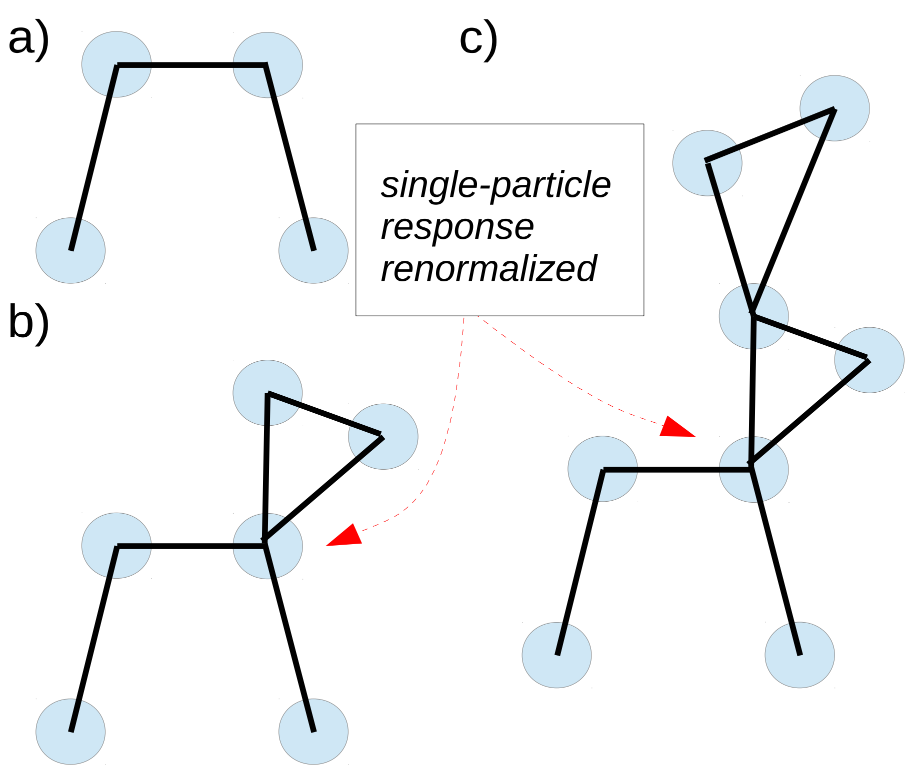


$$\mathbf{v}\left(\mathbf{r}\right) \sim \mathbf{G}\left(\mathbf{r}\right)\cdot\mathbf{F}$$

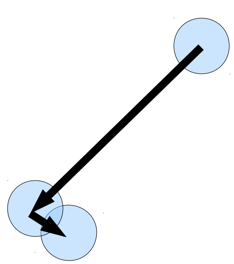
Beenakker-Mazur method (1983)

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 and Mazur scheme

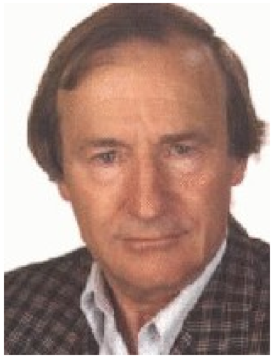
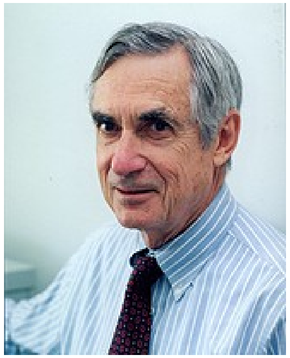
Beenakker and Mazur scheme – expansion in density fluctuations (1983). The most comprehensive statistical physics theory for short times properties of suspension nowadays

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

No satisfactory statistical physics method including the above three features

Lubrication important!

1982 – problem of long-range HI solved


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

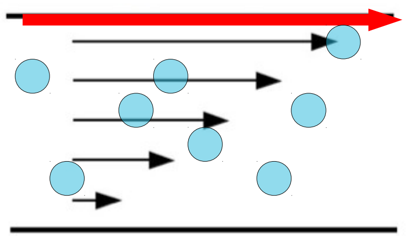
Received August 24, 1981

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

Response of suspension (effective viscosity)

Viscosity by relation between pressure tensor and average flow of suspension (Landau):



average velocity field of suspension

$$\langle \mathbf{f}(\mathbf{R}) \rangle = \int d^3 r' \mathbf{T}^{irr}(\mathbf{R}, \mathbf{r}') \langle \mathbf{v}(\mathbf{r}') \rangle$$

average surface force (dipole)

viscosity operator

Effective viscosity coefficient is given directly by the response operator T^{irr}

Felderhof, Ford, Cohen – cluster expansion (1982)

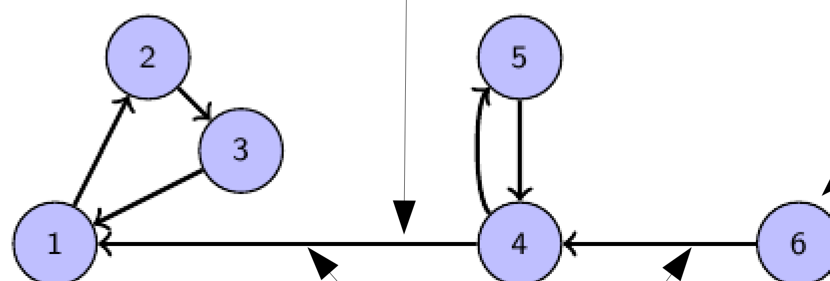
$$T^{irr} = \sum_{g=1}^{\infty} \sum_{C_1 \ldots C_g} \int dC_1 \ldots dC_g b(C_1 | \ldots | C_g) S_I(C_1) G \ldots G S_I(C_g)$$

block distribution function (configurations of particles)

Oseen tensor: $G = \frac{1}{8\pi\eta} \frac{\mathbf{1} + \hat{\mathbf{r}}\hat{\mathbf{r}}}{r}$

Example of scattering sequence (many-body):

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



$M(6)$

short range hydrodynamic interactions (strong interactions of close particles)

long range hydrodynamic interactions

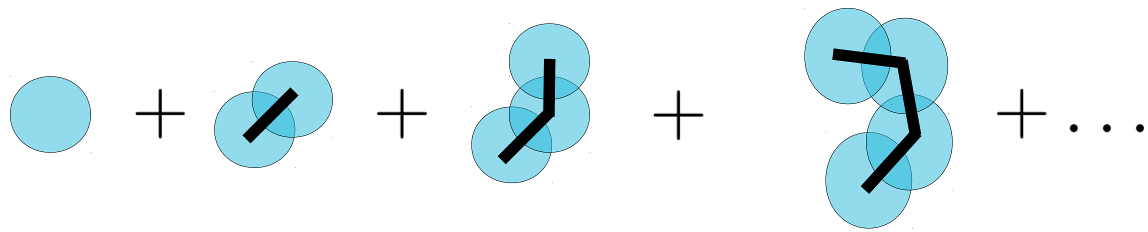
$$S_I(123) G S_I(45) G S_I(6)$$

$$C_1 \equiv 123 \quad C_2 \equiv 45 \quad C_3 \equiv 6$$

Problem with long-range HI solved

Felderhof, Ford, Cohen – microscopic explanation of Clausius-Mossotti (Saito) formula (1983)

$\mathbf{T}^{irr} \leftarrow$



$$\langle \mathbf{f}(\mathbf{R}) \rangle = \int d^3 r' \mathbf{T}^{irr}(\mathbf{R}, \mathbf{r}') \langle \mathbf{v}(\mathbf{r}') \rangle$$

The following definition

$$\mathbf{T}^{irr}_{CM} = \mathbf{T}^{irr} \left(1 + [h\mathbf{G}]\, \mathbf{T}^{irr} \right)^{-1}$$

and approximate closure relation

$$\mathbf{T}^{irr}_{CM} \approx n_1 \hat{\mathbf{M}}$$

lead to Saito formula

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

Our approach – renormalization of the propagator

Cluster expansion (1982):

short-range hydrodynamic interaction

$$T^{irr} = \sum_{g=1}^{\infty} \sum_{C_1 \ldots C_g} \int dC_1 \ldots dC_g b(C_1|\ldots|C_g) S_I(C_1) G \ldots G S_I(C_g)$$

block distribution function
(configurations of particles)

Oseen tensor (pure liquid):

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

Ring expansion (2011):

$$T^{irr} = \sum_{g=1}^{\infty} \sum_{C_1 \ldots C_g} \int dC_1 \ldots dC_g H(C_1|\ldots|C_g) S_I(C_1) G_{\text{eff}} \ldots G_{\text{eff}} S_I(C_g)$$

block correlation function
(configurations of particles);
H=b for g=1,2,
H different from b for g>2.

Effective Green function:

$$\mathbf{G}_{\text{eff}}(\mathbf{r}) \sim \frac{\eta}{\eta_{\text{eff}}} \mathbf{G}(\mathbf{r})$$

Two approximation schemes

Constructing approximate method by carrying over approximation from cluster expansion to ring expansion with the following modification:

$$G \Longrightarrow G_{\text{eff}}$$

Clausius-Mossotti (Saito) approximation $\Longrightarrow$ *Generalized Clausius-Mossotti approximation*

(two-body hydrodynamic interactions incomplete – the same as in Beenakker and Mazur scheme)

to be published soon

One-ring approximation (fully takes into account two-body hydrodynamic interactions)

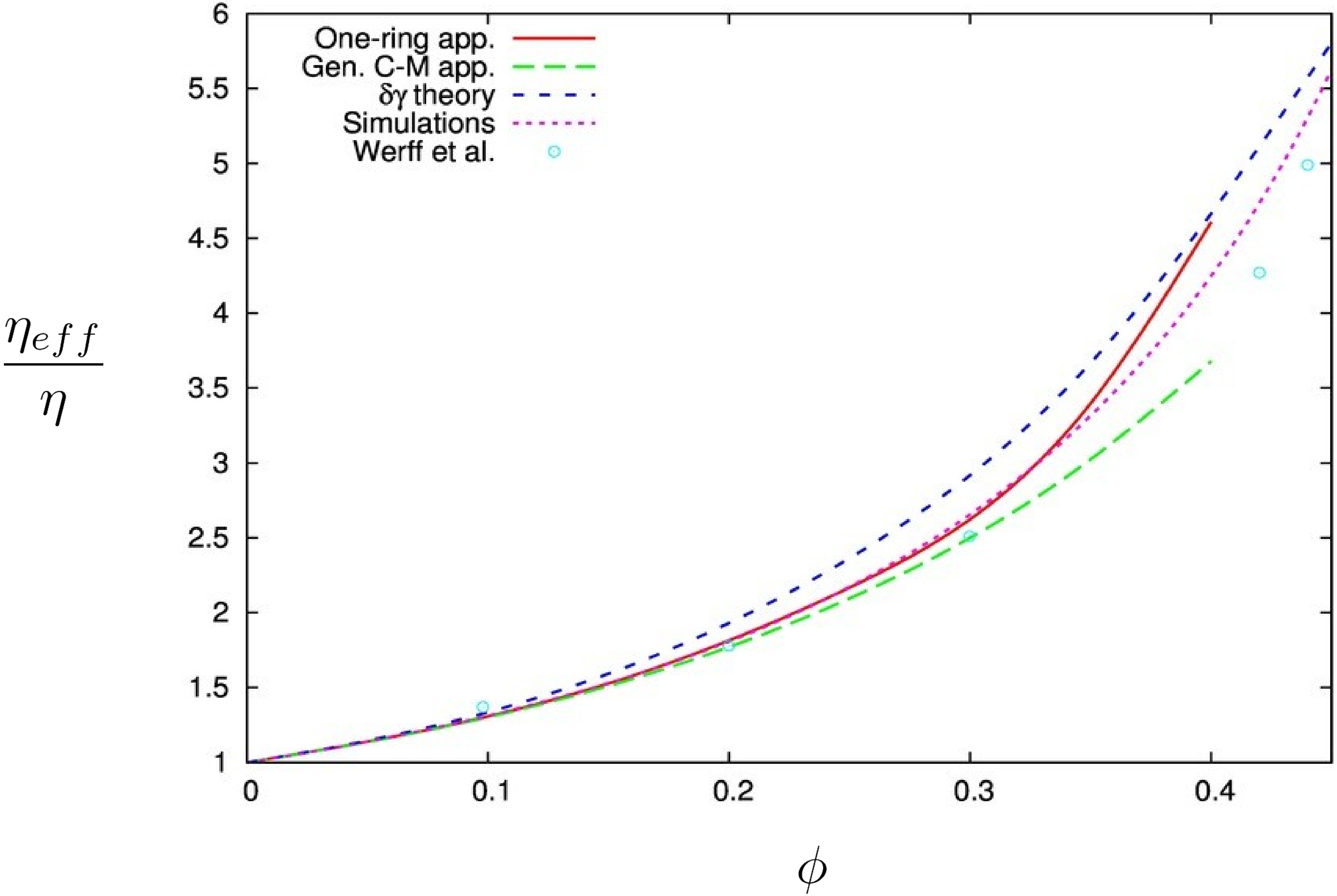
Input:

-volume fraction

-two-body correlation function (PY); (three-particle correlation function by two body correlation function (Kirkwood))

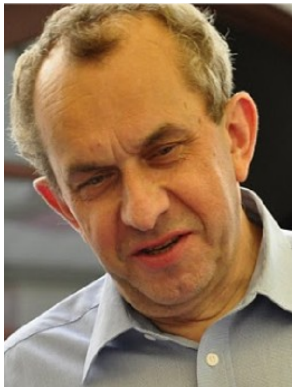
-two-body hydrodynamic interactions

Effective viscosity



Summary

- Long-range, many-body hydrodynamic interactions and strong interactions of close particles are important in suspensions (still an open problem)
- Rigorous ring expansion can grasp all of the above features (opposite to δγ)
- Two approximation schemes for transport coefficients:
  - generalized Clausius-Mossotti approximation (two-body hydrodynamic interactions not fully taken; comparable to δγ scheme) – to be published soon
  - one-ring approximation (full two-body hydrodynamic interactions, much better accuracy than hitherto theoretical methods in comparison to numerical simulations for volume fraction less than 35%)



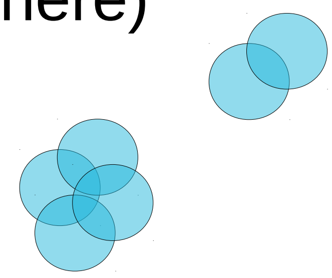
in colaboration with Bogdan Cichocki, Univeristy of Warsaw

Outlook

- Straightforward generalization for different suspensions of spherical particles (droplets, spherical polymers) with different distributions (charged particles)

- polidisperse suspensions

- suspension of nonspherical particles (i.e. double sphere)

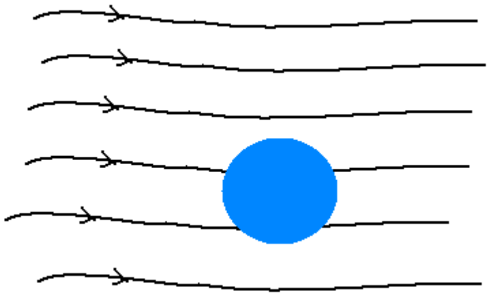


Single particle

Lamb (1895) $\mathbf{v}^{+}_{lm\sigma}(\mathbf{r})$

$$l = 1, 2, \ldots, \infty$$
$$m = -l, \ldots, l$$
$$\sigma = 0, 1, 2$$

Single particle in ambient flow $\mathbf{v}_0\left(\mathbf{r}\right)$



$$\mathbf{f}_1\left(\mathbf{r}\right) = \int d\mathbf{r}'\mathbf{M}\left(\mathbf{r}-\mathbf{R}_1, \mathbf{r}'-\mathbf{R}_1\right)\mathbf{v}_0\left(\mathbf{r}'\right)$$

Single particle operator
(Felderhof 1976)

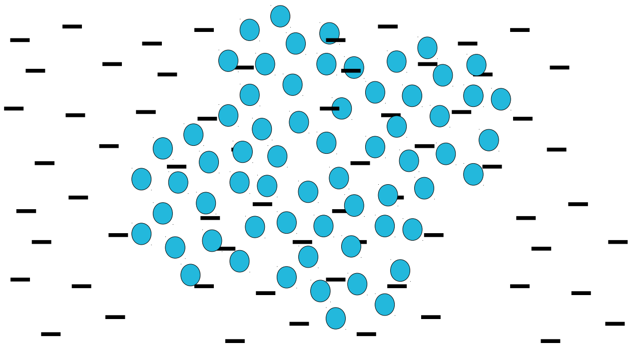
Surface force density
(Cox Brenner (1967); Mazur, Bedeaux (1974))

$$\mathbf{v}\left(\mathbf{r}\right) = \mathbf{v}_0\left(\mathbf{r}\right) + \int d^3\mathbf{r}'\mathbf{G}\left(\mathbf{r}-\mathbf{r}'\right)\cdot\mathbf{f}_1\left(\mathbf{r}'\right)$$

Oseen tensor:

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

Suspension



Ambient flow for the particle i in suspension:

$$\mathbf{v}_i\left(\mathbf{r}\right) = \mathbf{v}_0\left(\mathbf{r}\right) + \sum_{j \neq i} \int d^3\mathbf{r}' \mathbf{G}\left(\mathbf{r} - \mathbf{r}'\right) \cdot \mathbf{f}_j\left(\mathbf{r}'\right)$$

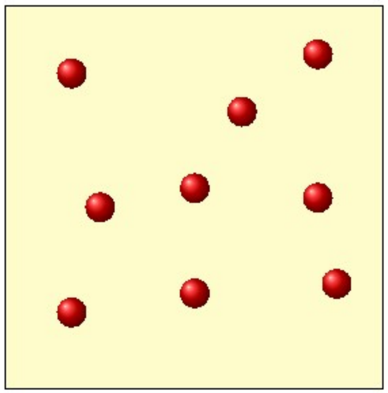
Single particle problem with modified ambient flow

$$\mathbf{f}_i = \mathbf{M}(i) \left(\mathbf{v}_0 + \sum_{i \neq j} \mathbf{G} \mathbf{f}_j \right)$$

Solution in the form of the following scattering series (hydrodynamic interactions)

$$\mathbf{f}_i = \left(\mathbf{M}(i) + \sum_{j \neq i} \mathbf{M}(i)\mathbf{G}\mathbf{M}(j) + \sum_{j \neq i} \sum_{k \neq j} \mathbf{M}(i)\mathbf{G}\mathbf{M}(j)\mathbf{G}\mathbf{M}(k) + \ldots \right) \mathbf{v}_0$$

Scattering series



ambient flow

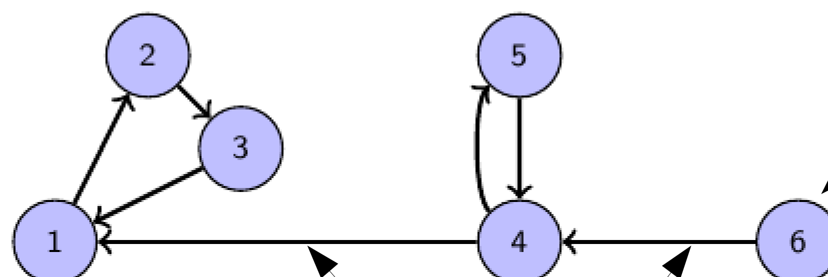
$$\mathbf{f}_i = \left(\mathbf{M}(i) + \sum_{j \neq i} \mathbf{M}(i)\mathbf{G}\mathbf{M}(j) + \sum_{j \neq i} \sum_{k \neq j} \mathbf{M}(i)\mathbf{G}\mathbf{M}(j)\mathbf{G}\mathbf{M}(k) + \ldots \right) \mathbf{v}_0$$

Single particle response operator

Green function for Stokes equations

Example of scattering sequence (many-body):

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



$M(6)$

short range hydrodynamic interactions
(strong interactions of close particles)

long range hydrodynamic interactions (nodal line)

block structure:

$$S_I(C_1) \text{———} S_I(C_2) \text{———} S_I(C_3)$$

$C_1 \equiv 123$ $C_2 \equiv 45$ $C_3 \equiv 6$

Response of suspension

(effective viscosity)

average velocity field of suspension

$$\langle f\rangle(\mathbf{R}) = \int d\mathbf{r}' T^{irr}(\mathbf{R},\mathbf{R}')\langle v\rangle(\mathbf{R}')$$

average surface dipole force

$$\langle v(\mathbf{R})\rangle = v_0(\mathbf{R}) + \int d\mathbf{r}' G(\mathbf{R},\mathbf{R}')\langle f(\mathbf{R}')\rangle$$

$$\langle f(\mathbf{R})\rangle = \int d^3\mathbf{R}' T(\mathbf{R},\mathbf{R}') v_0(\mathbf{R}')$$

Relation between T *and* T^{irr} *operators:*

$$T = T^{irr}\left(1 - GT^{irr}\right)^{-1}$$

Effective viscosity coefficient is given directly by the response operator T^{irr}

Macroscopic description

Average force density:

$$\langle f(\mathbf{R})\rangle \equiv \left\langle \sum_i f_i \delta(\mathbf{R}-i) \right\rangle$$

Average over probability distribution for configurations of particles, thermodynamic limit

$$\langle f(\mathbf{R})\rangle = \int d^3\mathbf{R}' T(\mathbf{R},\mathbf{R}')\, v_0(\mathbf{R}')$$

Response operator for suspension in ambient flow

$$T = \sum_{b=1}^{\infty} \sum_{C_1 \dots C_b} \int dC_1 \dots dC_b \; n(C_1 \dots C_b)\, S_I(C_1) G \dots G S_I(C_b)$$

s-particle distribution functions