Homogenization theory in complex liquids

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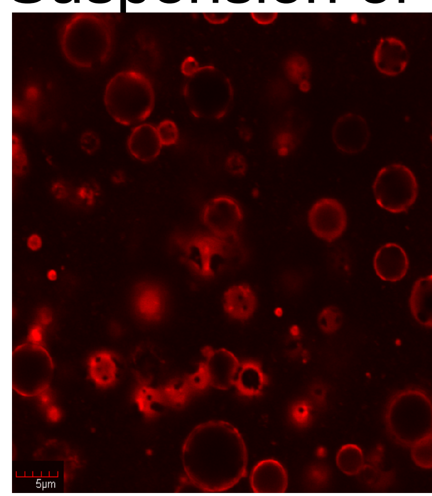
Introduction – complex liquids

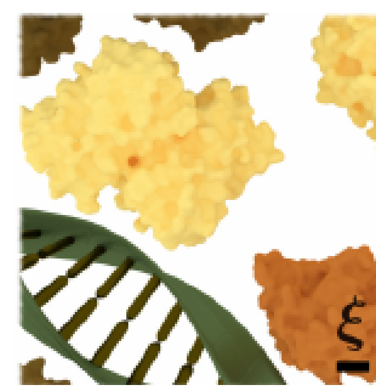
Complex liquid: a liquid with immersed macromolecules (polymers, big spherical particles, proteins)

Cornflour in water:

Suspension of spherical particles (~ milk)



Cell cytoplasm



Homogenization

Finding effective (averaged) description of system with inhomogeneities on microscopic scale

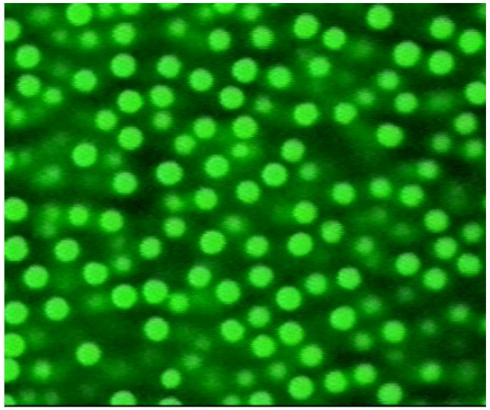
Equations for cornflour – seems complicated, nonlinear

stirring milk in a glass – flow similar to water but different viscosity

Homogenization in on of the simplest complex liquid: suspensions of hard spheres.

Homogenization – the simplest case

Suspension of identical
spherical particles

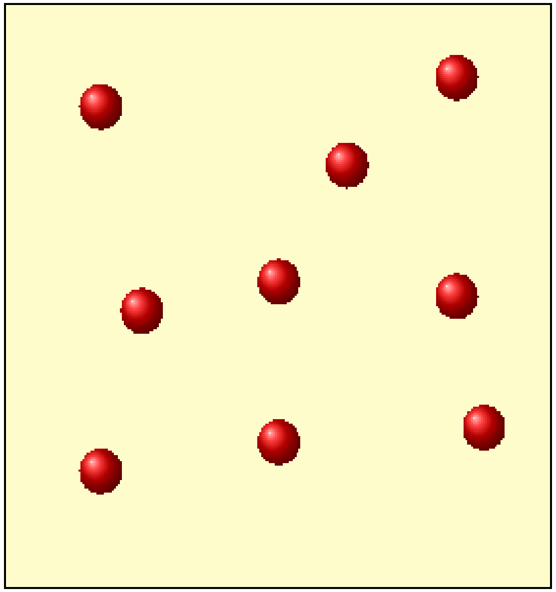


Effective viscosity

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,

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

e.g. shear flow

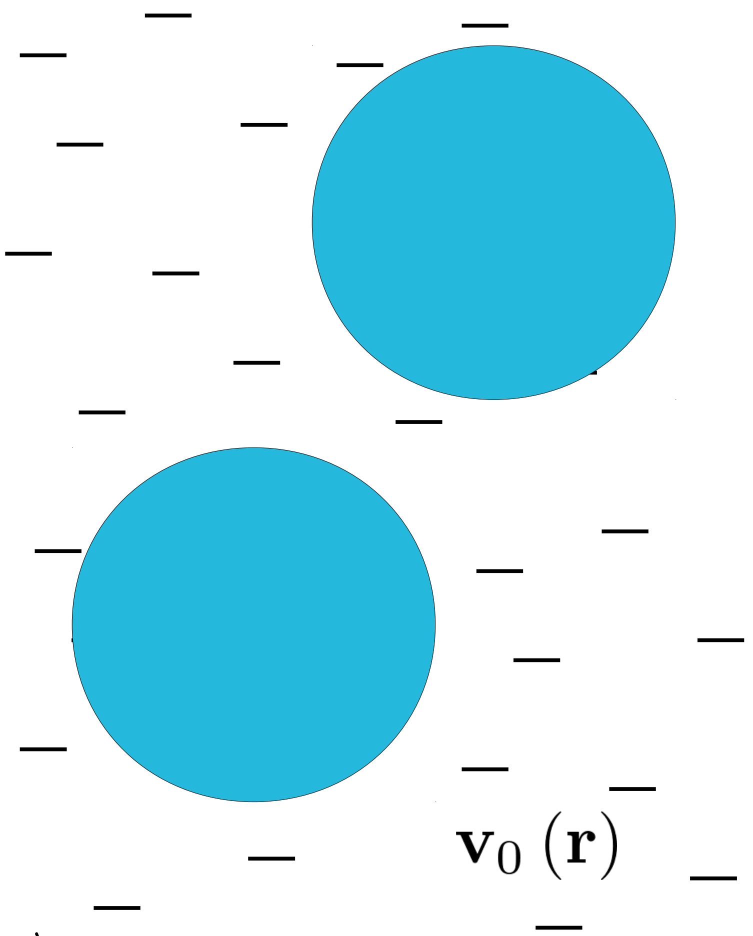
Effective viscosity

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

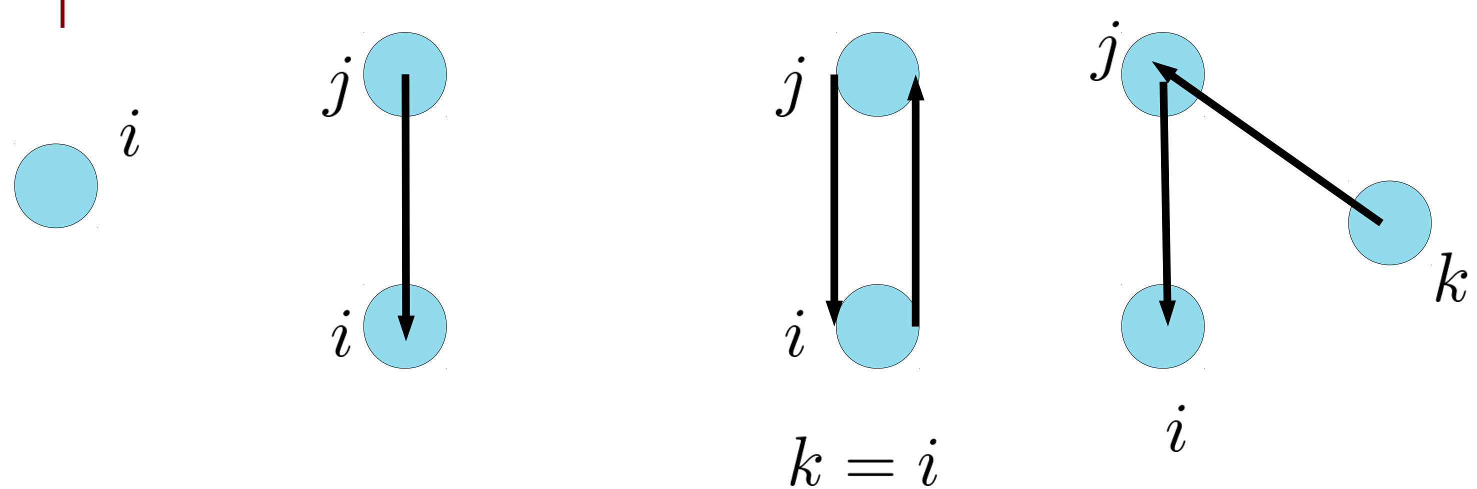


Effective viscosity from relation between $\langle \mathbf{f} \rangle$ and $\langle \mathbf{v} \rangle$

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

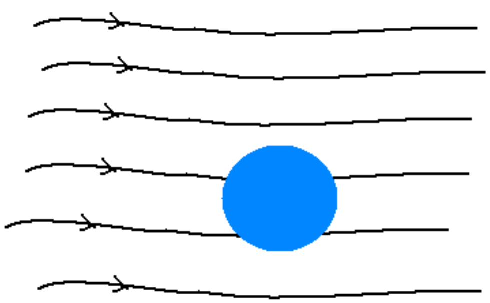
Transport properties – history and scattering series

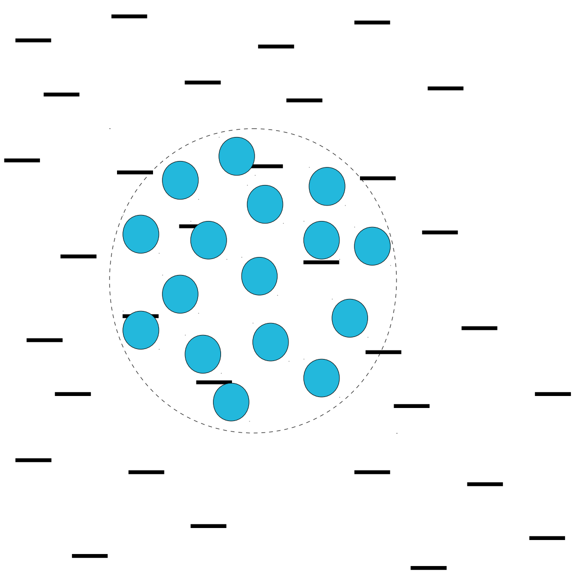
Einstein 1905
(corrected):

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

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

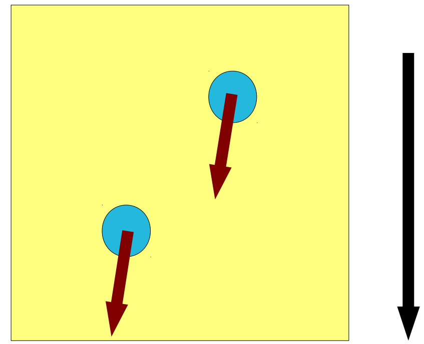
Single particle in ambient (shear) flow $\mathbf{v}_0(\mathbf{r})$

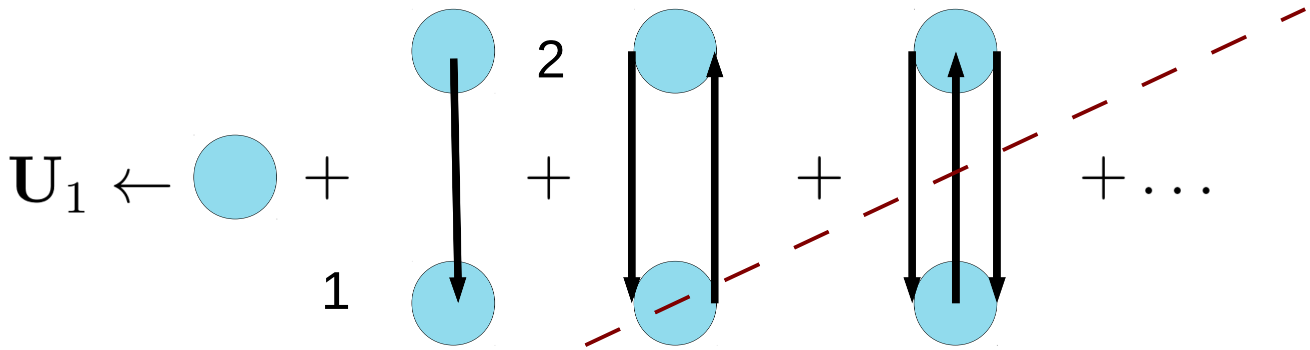


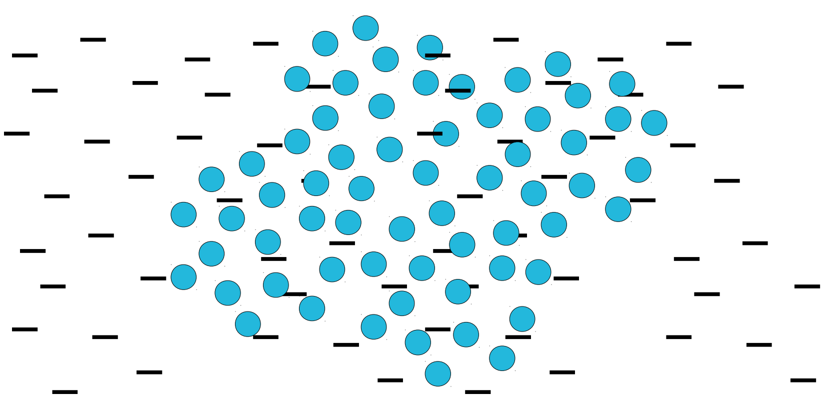


- Spherical cloud of particles
- Hydrodynamic interactions neglected
  (no reflections, single particle)

Hydrodynamic interactions – Smoluchowski (1911)





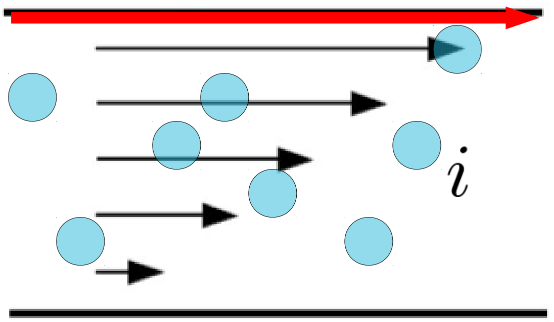


$$\int d^3r \left|\mathbf{G}(\mathbf{r})\right| = \infty$$

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

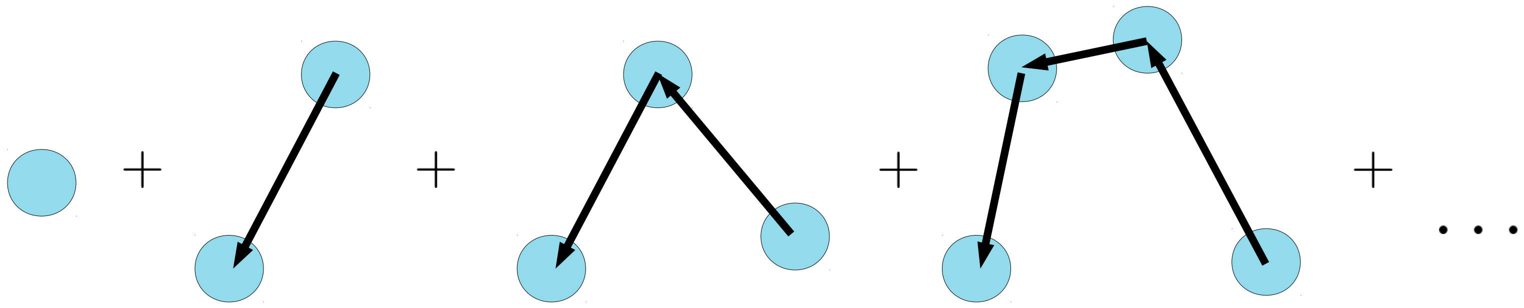
Well defined expression for effective viscosity?

Beyond diluted suspensions



Saito (1950):

-extension of Einstein work on mean-field level



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

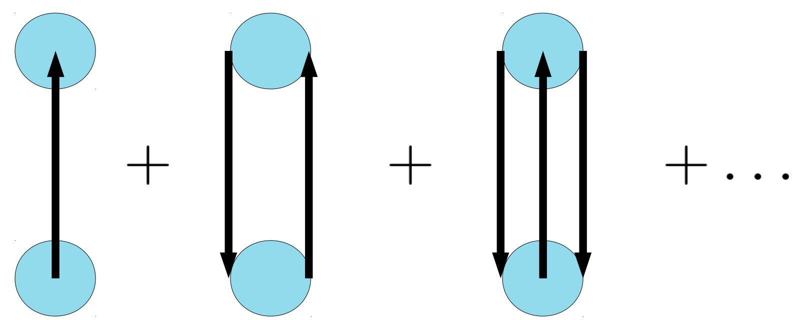
vanishes when two particles overlap

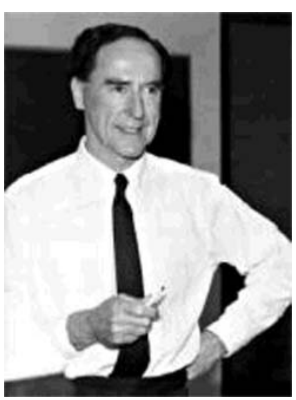
$$\frac{\eta_{eff}}{\eta} = \frac{1 + \frac{3}{2}\phi}{1 - \phi}$$

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)

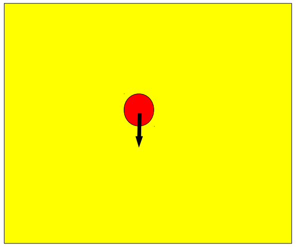
Problem with long-range HI still not solved in 1972

Hydrodynamic interactions

Many-body character

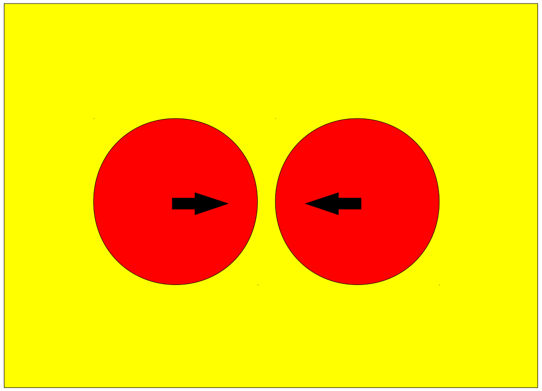
two-body approximation relevant for volume fractions less than about 5%

Long-range character



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

Strong interactions of close particles



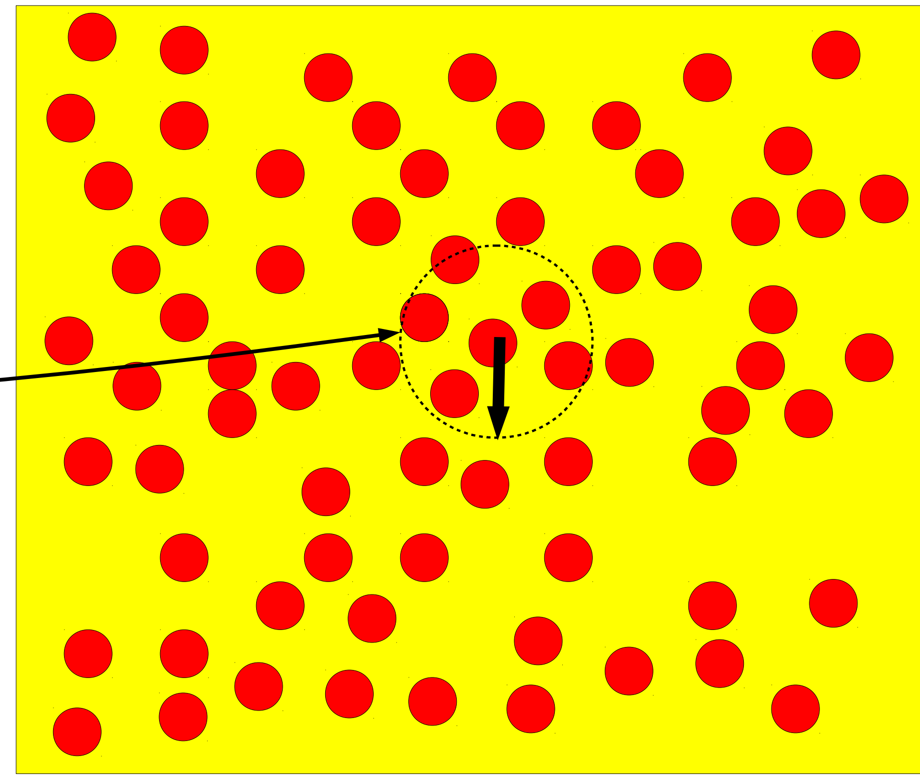
For constant velocities
asymptotically infinite drag force
(Jeffrey, Onishi (1984))

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

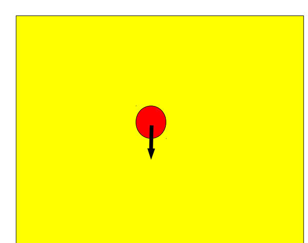
$$\mathbf{v}\left(\mathbf{r}\right) \sim \mathbf{G}_{\text{eff}}\left(\mathbf{r}\right)\mathbf{F}$$



effective Green function
(effective propagator):

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

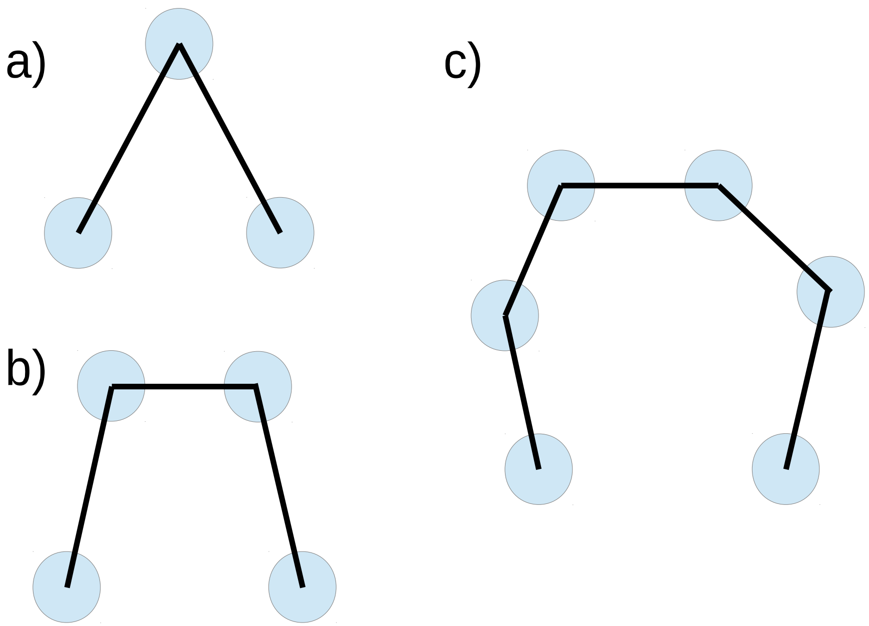
at the distance

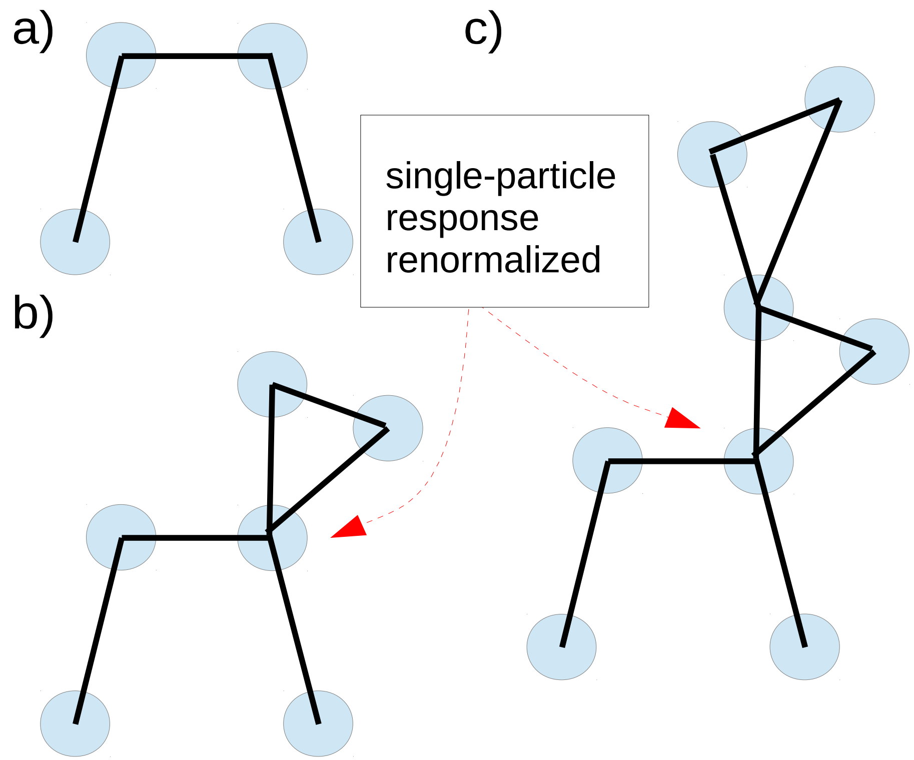


$$\mathbf{v}\left(\mathbf{r}\right) \sim \mathbf{G}\left(\mathbf{r}\right)\cdot\mathbf{F}$$

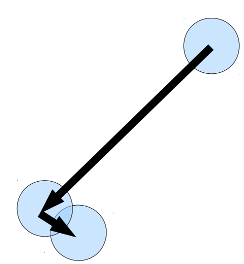
Beenakker-Mazur method (1983)

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

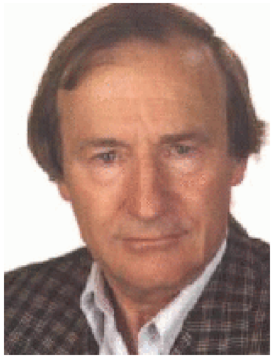
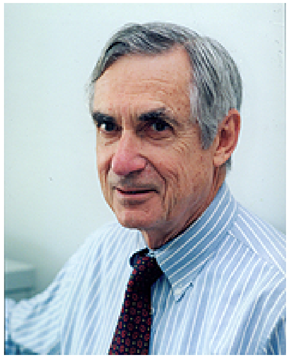
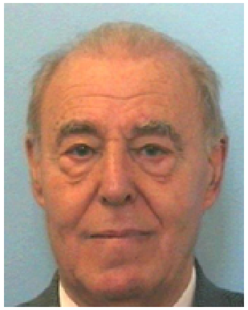




No correlations in position between particles in the above resummed terms



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

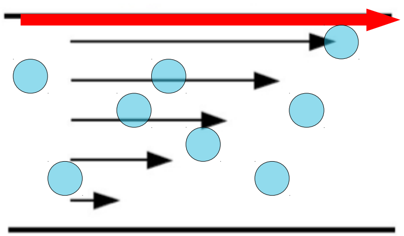
We derive a cluster expansion for the electric susceptibility kernel of a dielectric suspension of spherically symmetric inclusions in a uniform background. This also leads to a cluster expansion for the effective dielectric constant. It is shown that the cluster integrals of any order are absolutely 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
(macroscopic quantity)

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

Felderhof, Ford, Cohen – cluster expansion (1982)

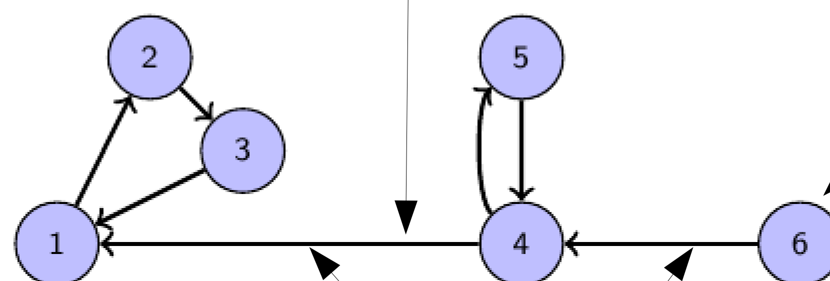
$$\mathbf{T}^{irr} = \sum_{g=1}^{\infty} \sum_{C_1 \ldots C_g} \int dC_1 \ldots dC_g b(C_1|\ldots|C_g) S_I(C_1) G \ldots G S_I(C_g)$$

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

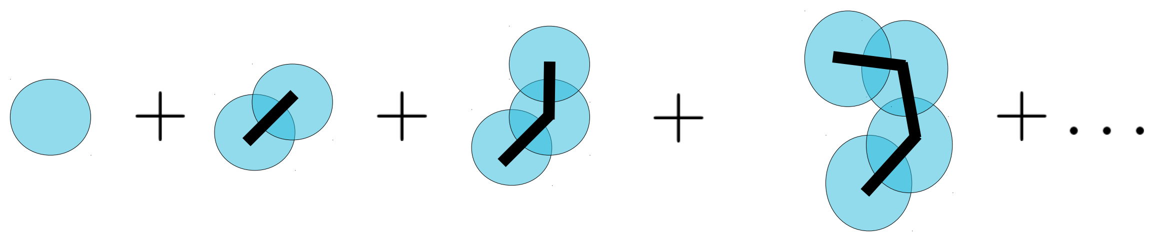
$$S_I(123)GS_I(45)GS_I(6)$$

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

Problem with long-range HI solved

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

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



leads to Saito formula

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

Our approach – renormalization of the propagator

Cluster expansion (FFC, 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):

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

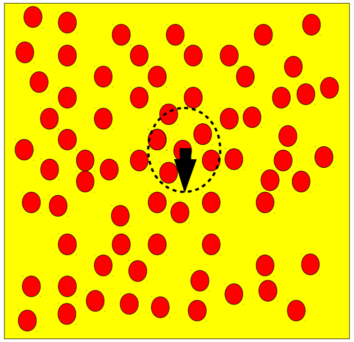
Ring expansion (2015)

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

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

Effective Green function:

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

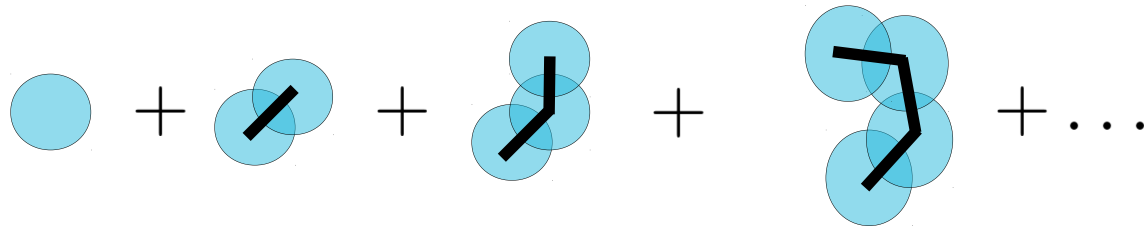


K. Makuch, Phys. Rev. E, 2015, 92, 04231

Two approximation schemes

Clausius-Mossotti (Saito) approximation:

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



when ‘renormalized’:

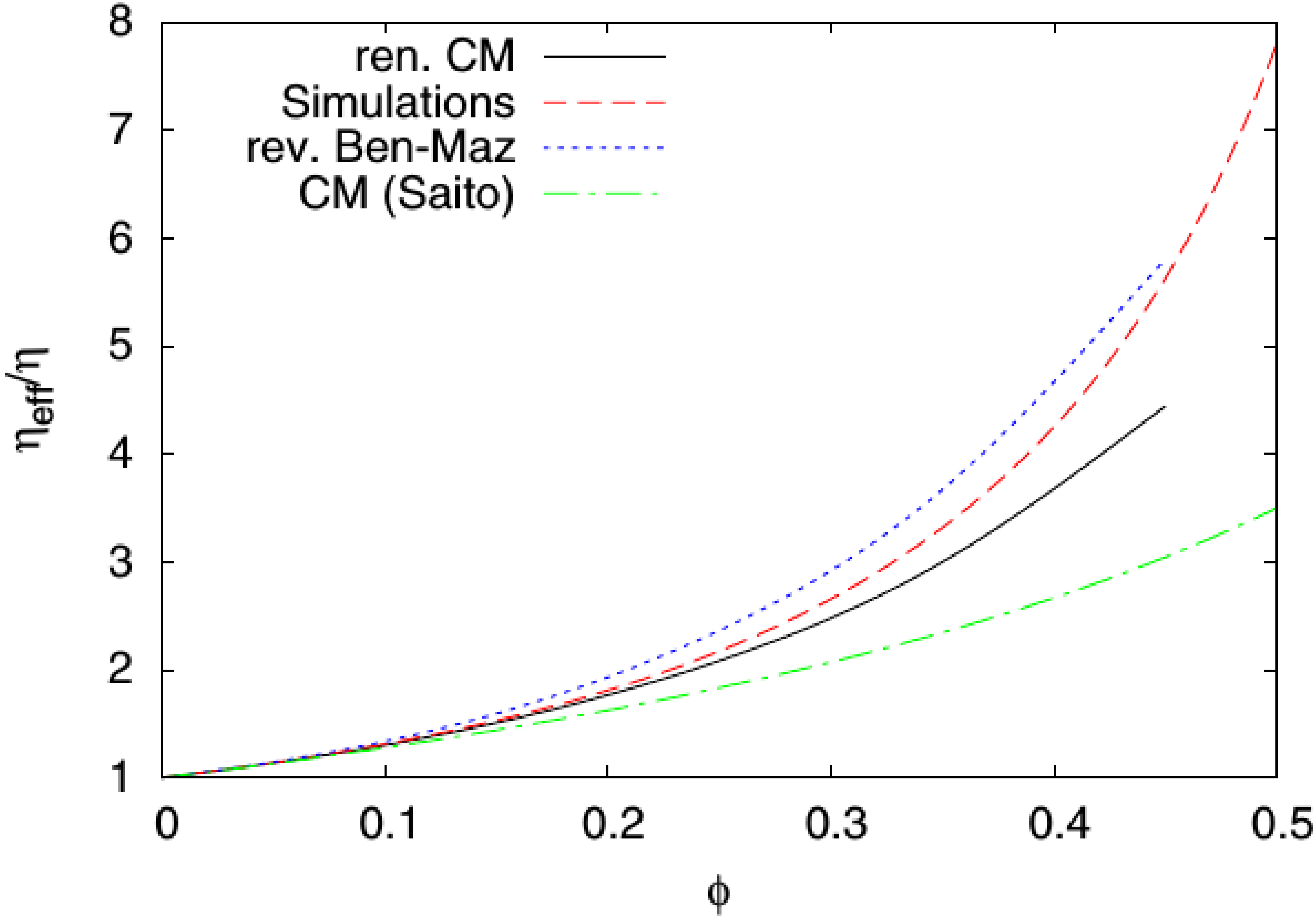
$$G \Longrightarrow G_{\mathrm{eff}}$$

leads to Renormalized Clausius-Mossotti approximation

K. Makuch, Phys. Rev. E, 2015, 92, 04231

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

Effective viscosity



K. Makuch, Phys. Rev. E, 2015, 92, 04231

Homogenization: state of the art 2017 and open question

Beenakker and Mazur scheme – expansion in renormalized density fluctuations (1983)
and
Renormalized Clausius-Mossotti approximation (2015):

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

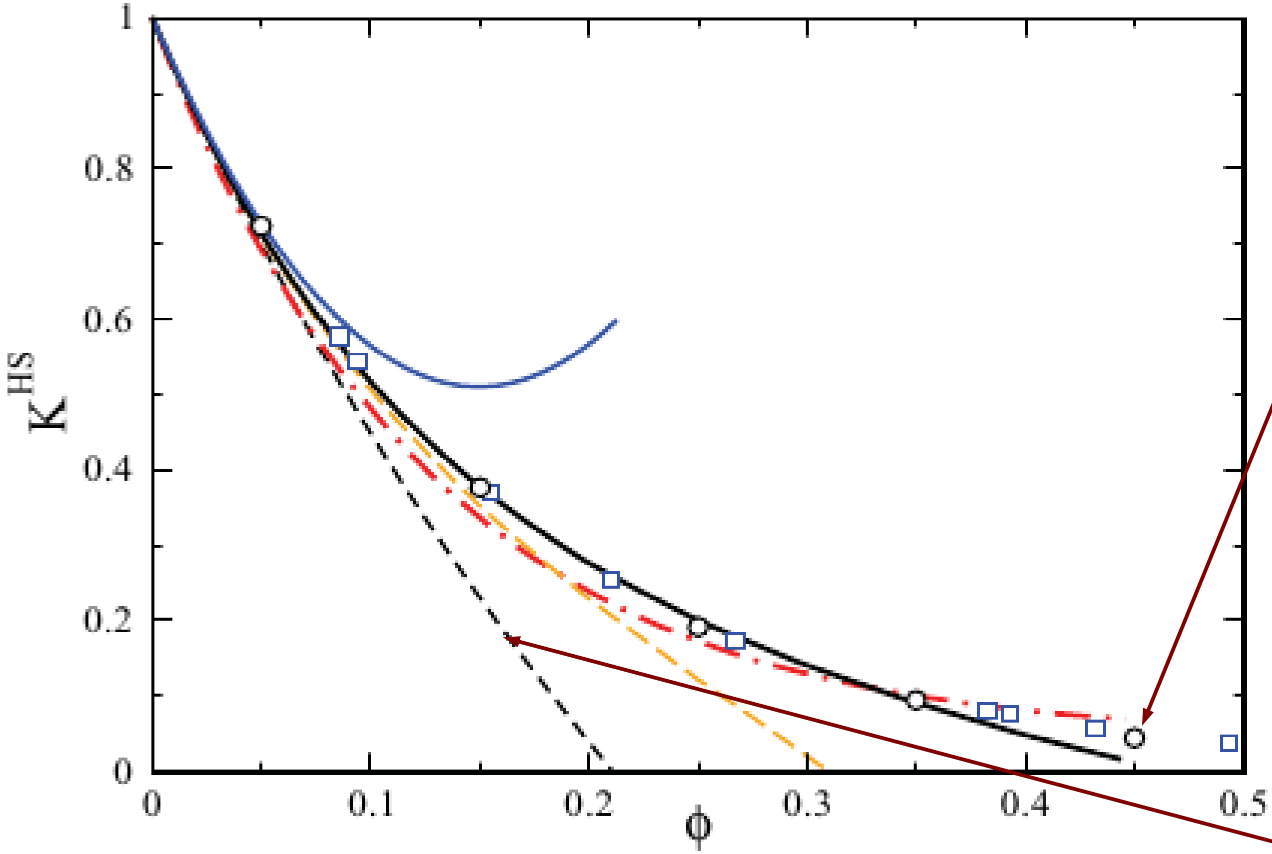
Currently there is no satisfactory statistical physics method including the above three features

Lubrication corrections important. How to take them into account?

It may be problematic...

Homogenization: open question – is it difficult?

Sedimentation coefficient for hard sphere suspension



volume fraction

numerical simulations
(close to experiments)

Heinen, M.; Banchio, A. & Nägele, G.
J. Chem Phys, 2011, 135, 154504

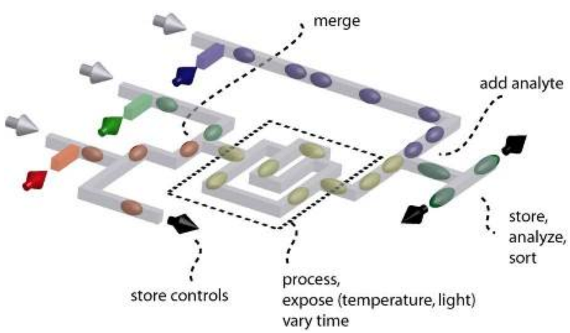
two-body approximation

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

Taking into account full two-body HI leads to unphysical results for low volume fractions (poorer approximation schemes give more 'physical' results)

Recent results – motivation

December 2015



Piotr Garstecki

+ ~20 group members

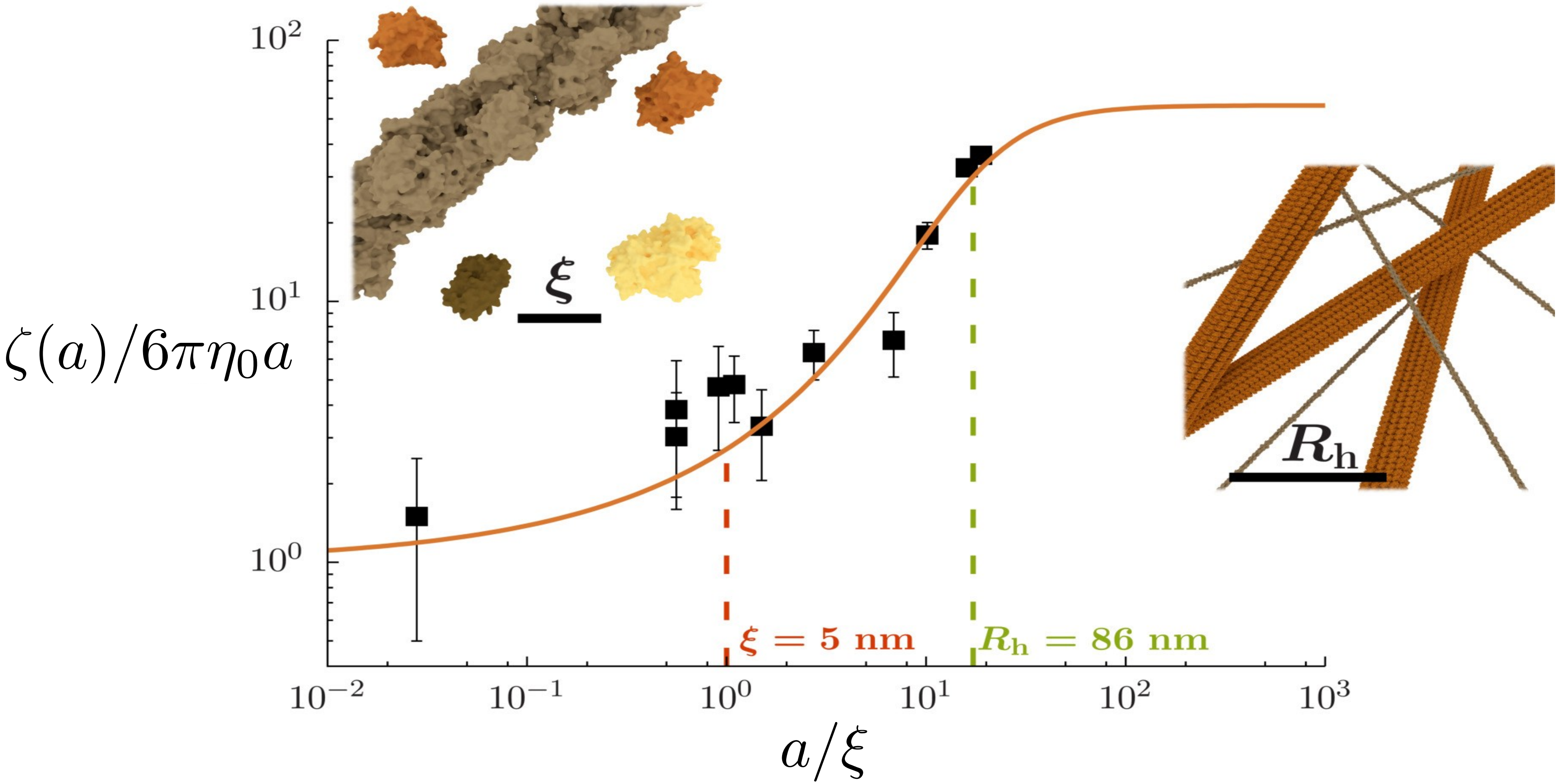
Robert Hołyst

Diffusion in biological systems and complex liquids
…..

+ ~20 group members

Friction coefficient inside HeLa cell cytoplasm

Friction coefficient: $\mathbf{F} = \zeta\,(a)\,\mathbf{U}$



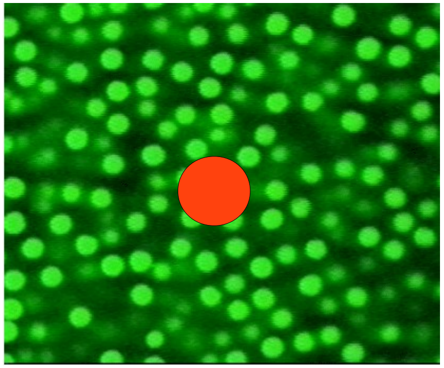
T Kalwarczyk et al. Nano letters, 11(5):21572163, 2011
M Kloster-Landsberg et al. Biophysical journal, 103(6):11101119, 2012
M K Daddysman et al. The Journal of Physical Chemistry B, 117(5):12411251, 2013.
Y Nakane et al. Analytical Methods, 4(7):19031905, 2012.

What are the equations describing dramatic change of friction for particles of different radii?

Stokes equations in <u>complex liquids</u> viscosity depends on scale:

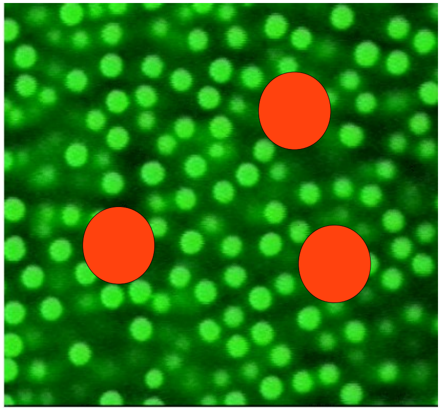
$$\begin{aligned} i\mathbf{k}p + k^2\eta(k)\,\hat{\mathbf{v}}(\mathbf{k}) &= 0, \\ \mathbf{k}\cdot\hat{\mathbf{v}}(\mathbf{k}) &= 0. \end{aligned}$$

$$\hat{\mathbf{G}}_{\mathrm{eff}}(\mathbf{k}) = \frac{1}{k^2\eta(k)}(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}})$$



What is the friction coefficient $\zeta(a)$?

$$\mathbf{F} = \zeta(a)\,\mathbf{U}$$

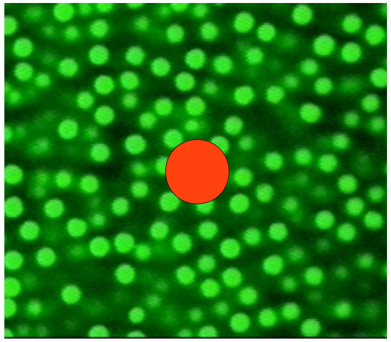


What is intrinsic viscosity coefficient $E(a)$?

$$\eta_{\mathrm{eff}} = \eta(0)\,(1 + E(a)\,\phi)$$

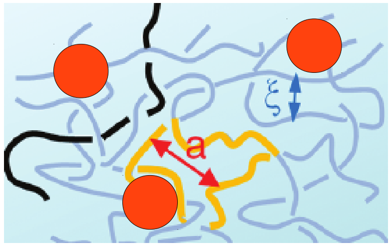
Intrinsic viscosity coefficient and Stokes' friction coefficient

Stokes law in complex liquids:



$$\zeta(a) = 3\pi^2 / \left(\int_0^\infty dk\, j_0(ka) / \eta(k) \right)$$

Intrinsic viscosity coefficient in complex liquids:



$$E(a) = -\frac{5}{2}\frac{1}{\eta(0)}\left[\frac{10}{3\pi}a^2\frac{d}{da}\int_0^\infty dk\,\frac{j_0(ak)}{\eta(k)} + \frac{4}{\pi}a\int_0^\infty dk\,\frac{j_2(ak)}{\eta(k)} + \frac{4a^2}{3\pi}\frac{d}{da}\int_0^\infty dk\,\frac{j_2(ak)}{\eta(k)}\right]^{-1}$$

Universal relation between friction and intrinsic viscosity coefficient:

$$E(a) = \frac{5}{12\pi\eta(0)\,a^2}\frac{\zeta(a)^2}{\frac{d\zeta(a)}{da}}$$

Experimental verification and verification by numerical simulations needed…

Conclusions from derived Stokes' law in complex liquids and prospects:

- Analytical results are possible for complex liquids with arbitrary wave-vector dependent viscosity
- For such a complex liquid the equations are still linear, but there is different single particle response and the Green function
- Possibility of numerical simulations of a big protein in crowded environment which will be represented by the wave-vector-dependent viscosity
- Currently work: on the homogenization method which takes into account also strong HI of close particles

In collaboration with

Bogdan Cichocki (University of Warsaw)

Robert Hołyst (IPC PAS)

Piotr Garstecki (IPC PAS)

Tomasz Kalwarczyk (IPC PAS)

John Brady (Caltech)