Structure and transport coefficients of charged and neutral colloidal particles

part II

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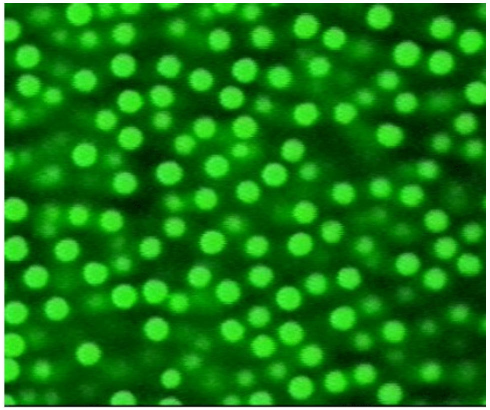
Introduction

Marco:
-structure of suspension
-transport properties



Transport properties (short time):
-effective viscosity η_{eff}
-sedimentation coefficient
-diffusion constant

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

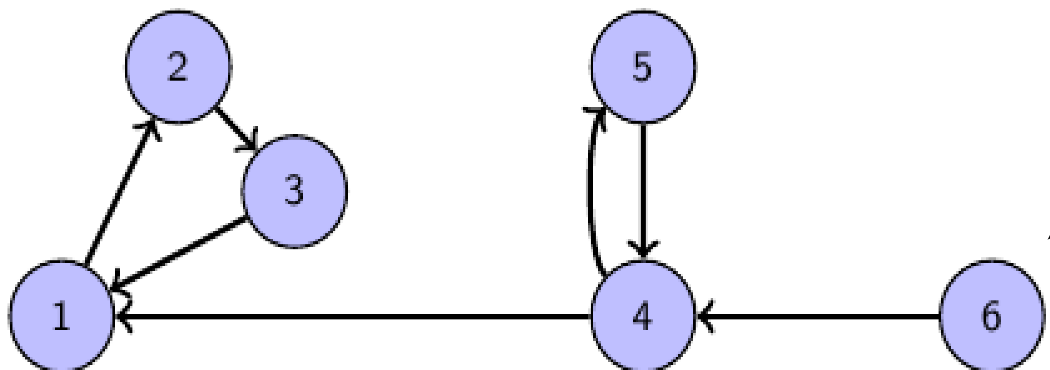
forces on surface of particle i: $\mathbf{f}_i(\mathbf{r}) \leftarrow \mathbf{v}_0(\mathbf{r})$

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):

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

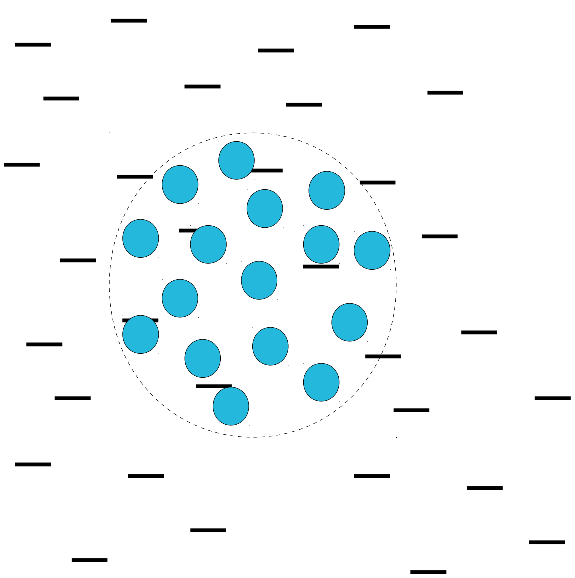
Probability distribution for position of particles: $p(1 \ldots N)$

Beginning of statistical physics considerations

Einstein 1906:

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

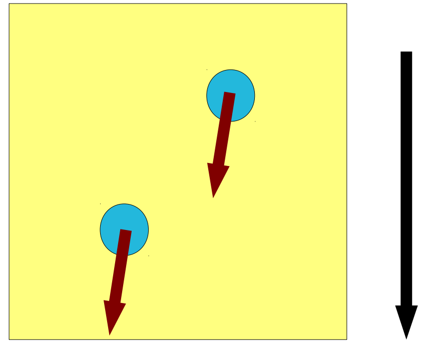
$$\phi = \frac{4}{3}\pi a^3 n$$

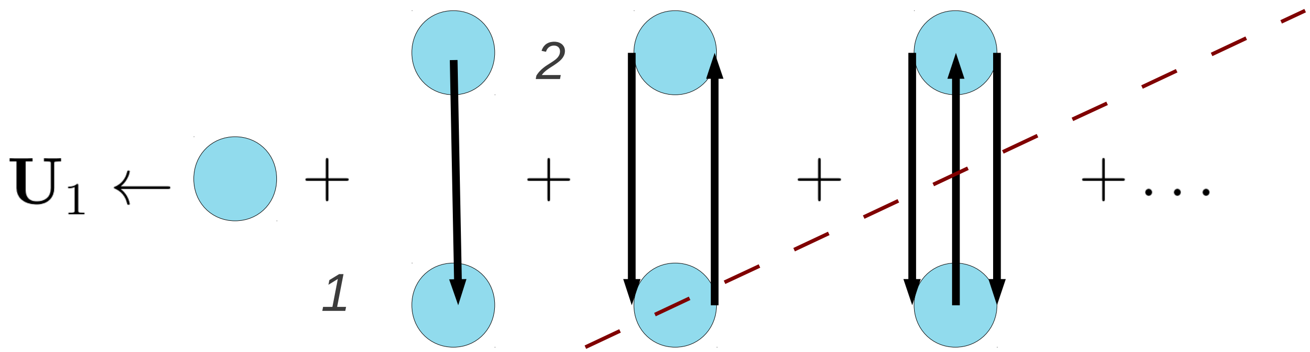


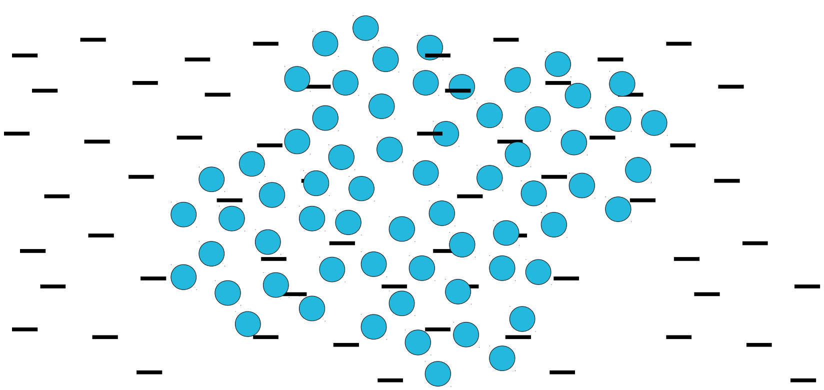
ambient (shear) flow $\mathbf{v}_0(\mathbf{r})$

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

Hydrodynamic interactions – Smoluchowski (1911)







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

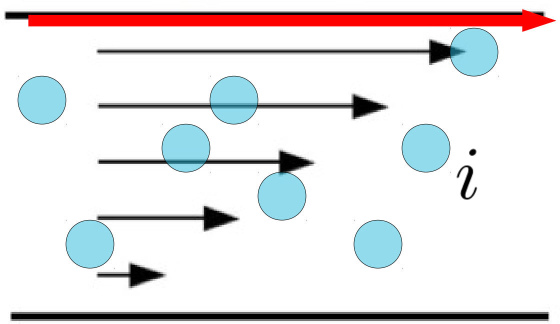
$$\mathbf{G}(\mathbf{r}) = \frac{1}{8\pi\eta}\frac{\mathbf{1} + \hat{\mathbf{r}}\hat{\mathbf{r}}}{r}$$

Well defined expression for effective viscosity?

Beyond diluted suspensions

Saito (1950):

-extension of Einstein work on mean-field level

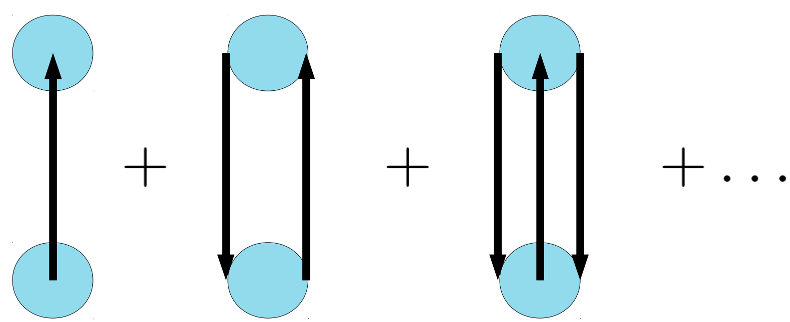


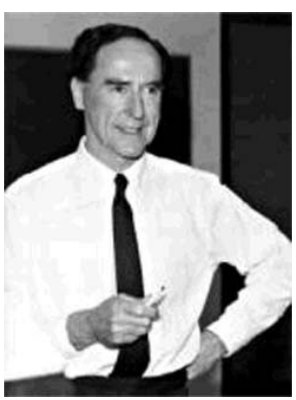
$$\frac{\eta_{eff}}{\eta} = \frac{1+\frac{3}{2}\phi}{1-\phi}$$

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

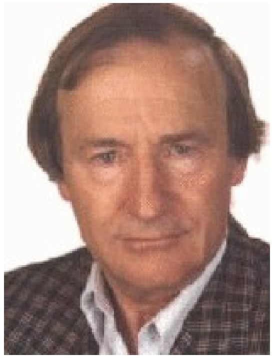
Batchelor, Green (1972): $a_2 \approx 5.2$

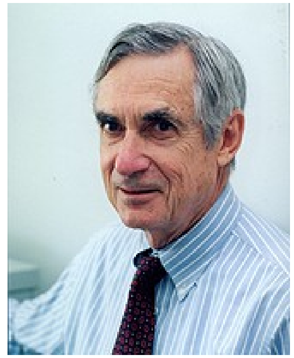
$$\int d^3r \left|\mathbf{G}(\mathbf{r})\right| = \infty$$

(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]

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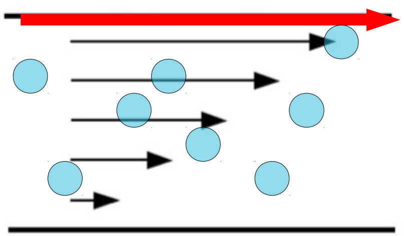
We derive a cluster expansion for the electric susceptibility kernel of a dielectric suspension of spherically symmetric inclusions in a uniform background. This also leads to a cluster expansion for the effective dielectric constant. It is shown that the cluster integrals of any order are absolutely 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 dissipation of energy (Einstein)
-by relation between pressure tensor and average flow of suspension (Landau)



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

average velocity field of suspension

average surface force (dipole)

viscosity operator

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

Felderhof, Ford, Cohen – cluster expansion (1982)

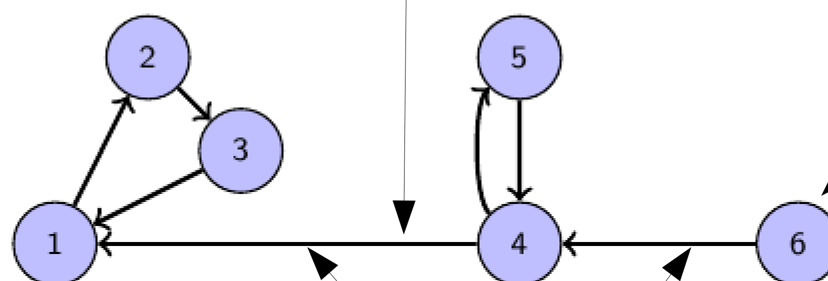
$$T^{irr} = \sum_{g=1}^{\infty} \sum_{C_1 \ldots C_g} \int dC_1 \ldots dC_g b(C_1|\ldots|C_g) S_I(C_1) G \ldots G S_I(C_g)$$

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

block distribution function
(configurations of particles)

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

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

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

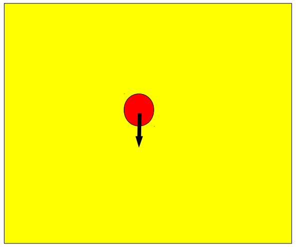
Problem with long-range HI solved

Hydrodynamic interactions

Many-body character

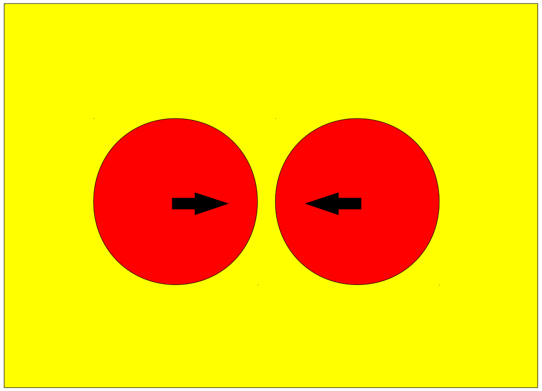
two-body approximation relevant for volume fractions less than about 5%

Long-range character



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

Strong interactions of close particles



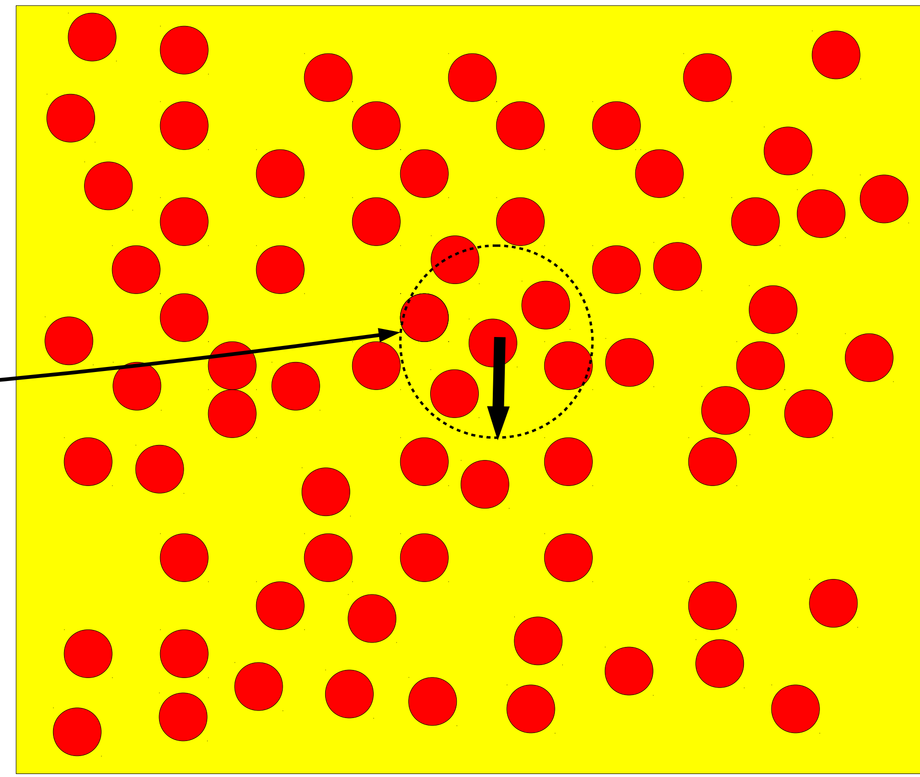
For constant velocities
asymptotically infinite drag force
(Jeffrey, Onishi (1984))

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

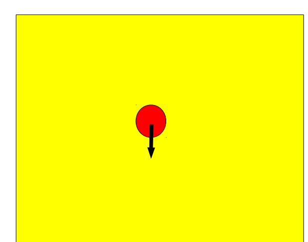
$$\mathbf{v}\left(\mathbf{r}\right) \sim \mathbf{G}_{\rm eff}\left(\mathbf{r}\right)\mathbf{F}$$



effective Green function (effective propagator):

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

at the distance



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

Beenakker 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!

Renormalization 2011

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):

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

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

Effective Green function:

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

Two approximation schemes

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

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

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

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

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

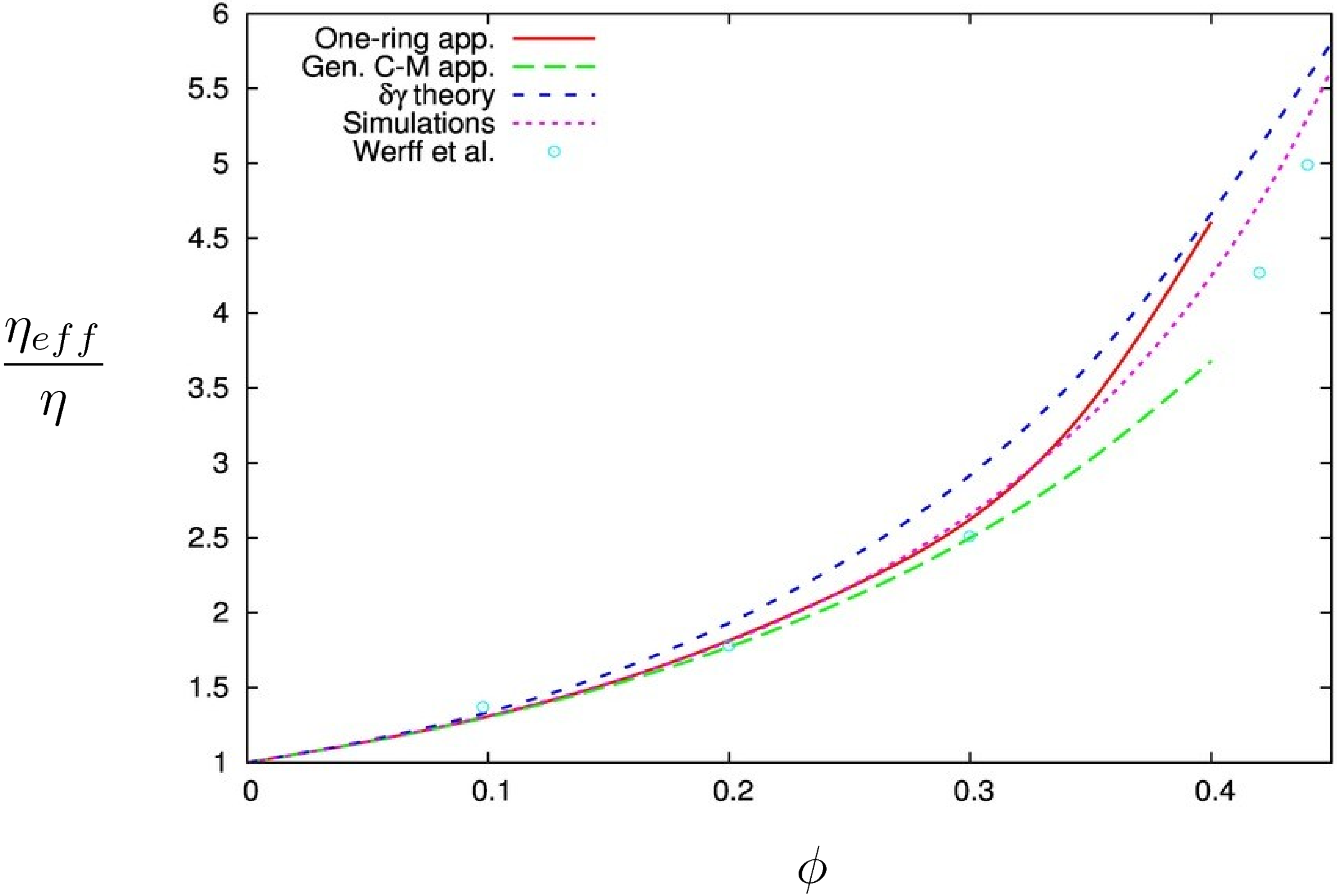
Input:

-volume fraction

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

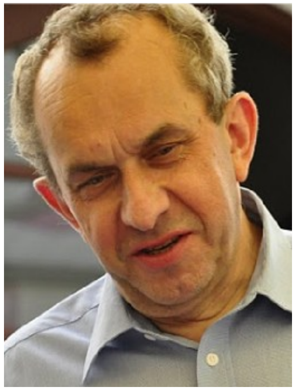
-two-body hydrodynamic interactions

Effective viscosity



Summary

- *Long-range, many-body hydrodynamic interactions and strong interactions of close particles are important in suspensions*
- *No method taking all of these features into consideration in literature*
- *Ring expansion for transport coefficients – can grasp all of three above features (good agreement with simulations up to 30% volume fraction)*



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