Macroscopic properties of suspensions of spherical particles

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INNOVATIVE ECONOMY
NATIONAL COHESION STRATEGY

FNP
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EUROPEAN UNION
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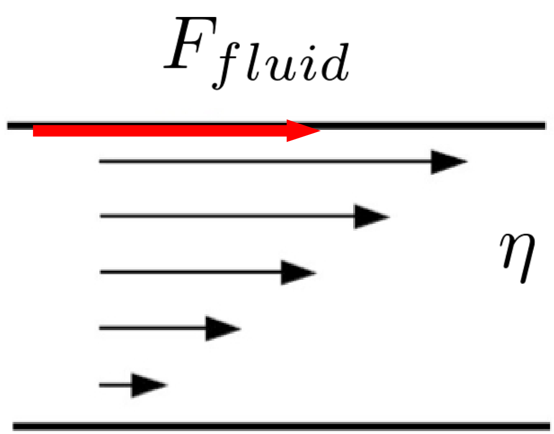
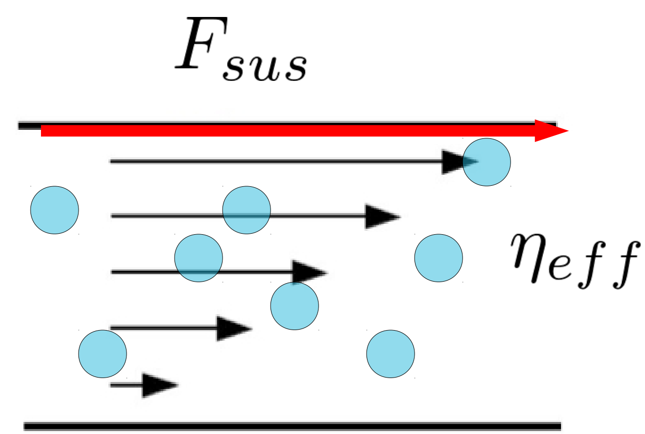
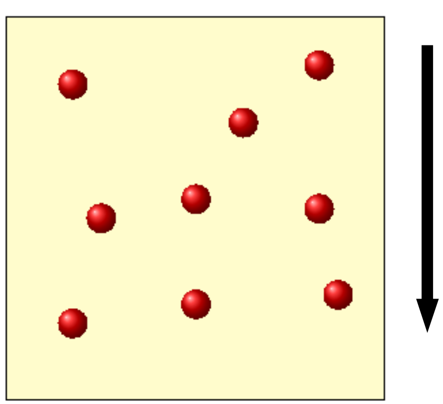
Viscosity, sedimentation, diffusion

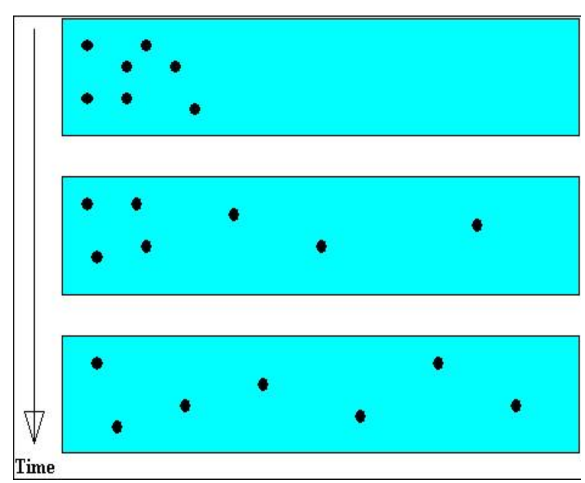




$$\frac{\eta_{eff}}{\eta} = \frac{F_{sus}}{F_{fluid}}$$



gravity field



Fick's law:

$$\vec{J} = -D\vec{\nabla}c$$

Beginning of microscopic considerations

Einstein 1906:

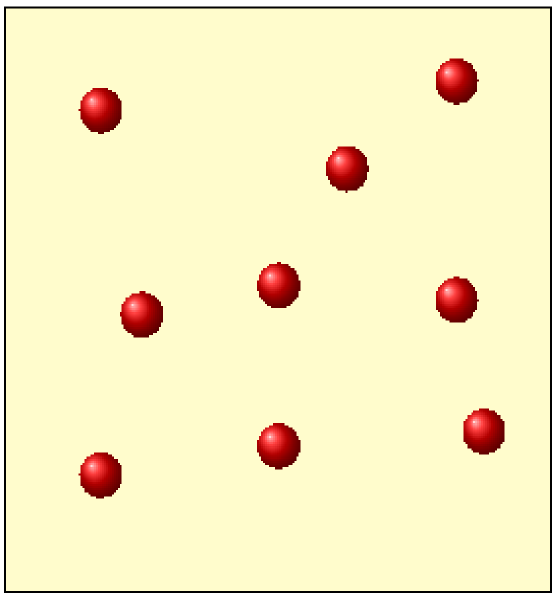
$$\eta_{eff} = \eta(1 + \frac{5}{2}\phi)$$

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

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

Hard-sphere suspension

Unbounded liquid,
N particles



Stokes equations:

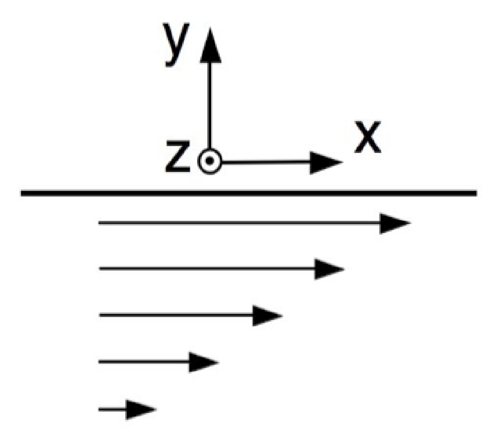
$$\begin{aligned} \nabla p(\mathbf{r}) - \eta \Delta \mathbf{v}(\mathbf{r}) &= 0 \\ \nabla \cdot \mathbf{v}(\mathbf{r}) &= 0 \end{aligned}$$

Stick boundary conditions,

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

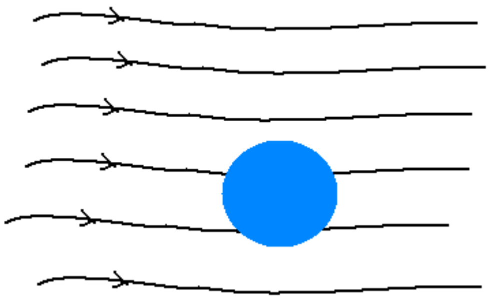
e.g. shear flow:

$$\mathbf{v}_0(\mathbf{r}) = \gamma y \hat{\mathbf{e}}_x$$



Single particle problem

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



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

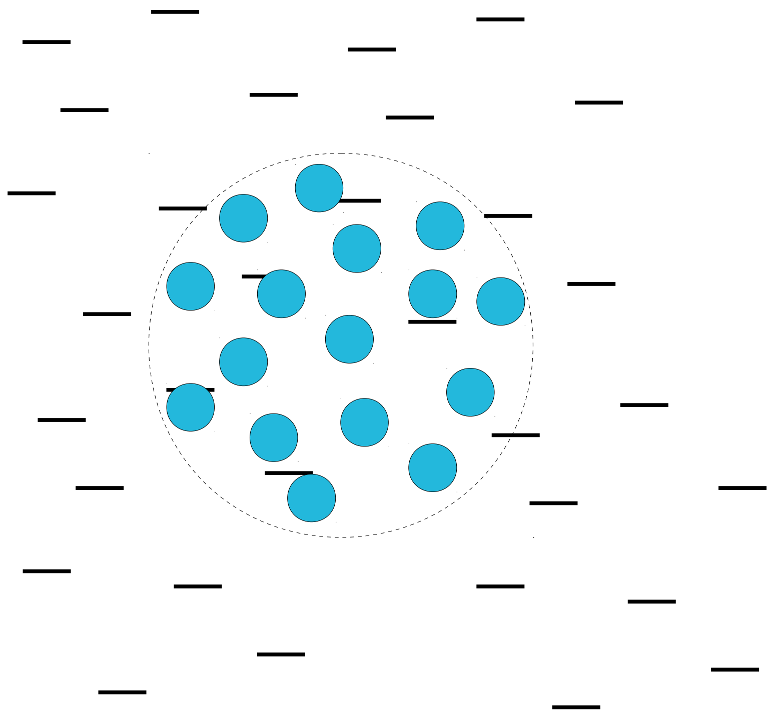
Single freely moving particle response operator

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

Oseen tensor:

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

Effective viscosity - Einstein

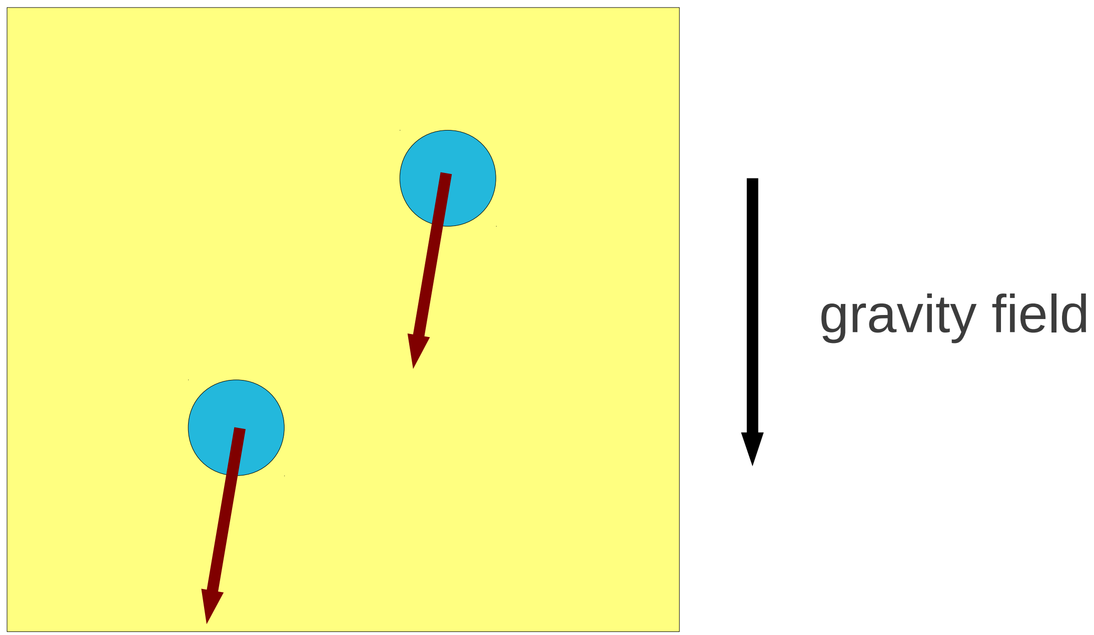


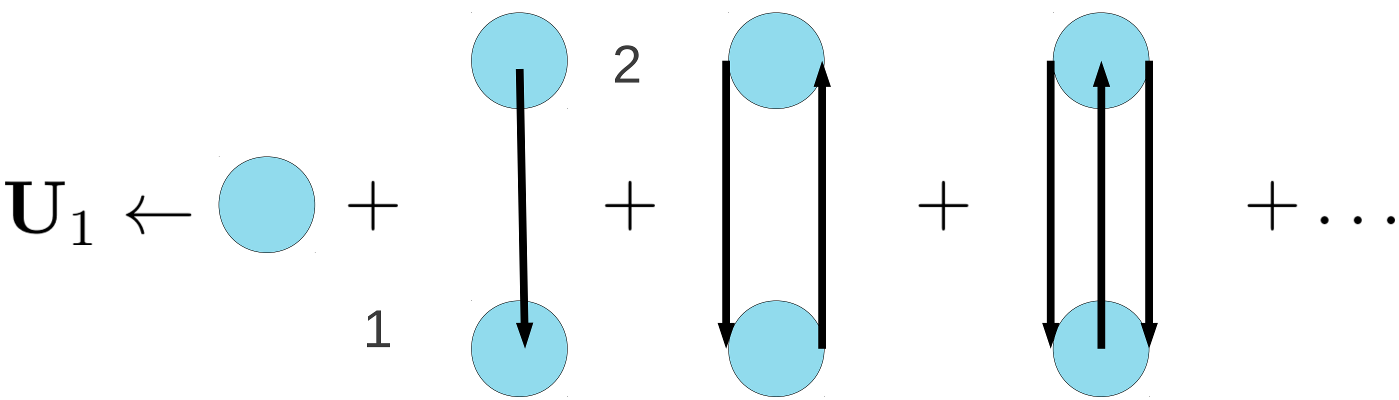
ambient flow $\mathbf{v}_0\left(\mathbf{r}\right)$

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

- Finite system
- Particles do not influence their movement

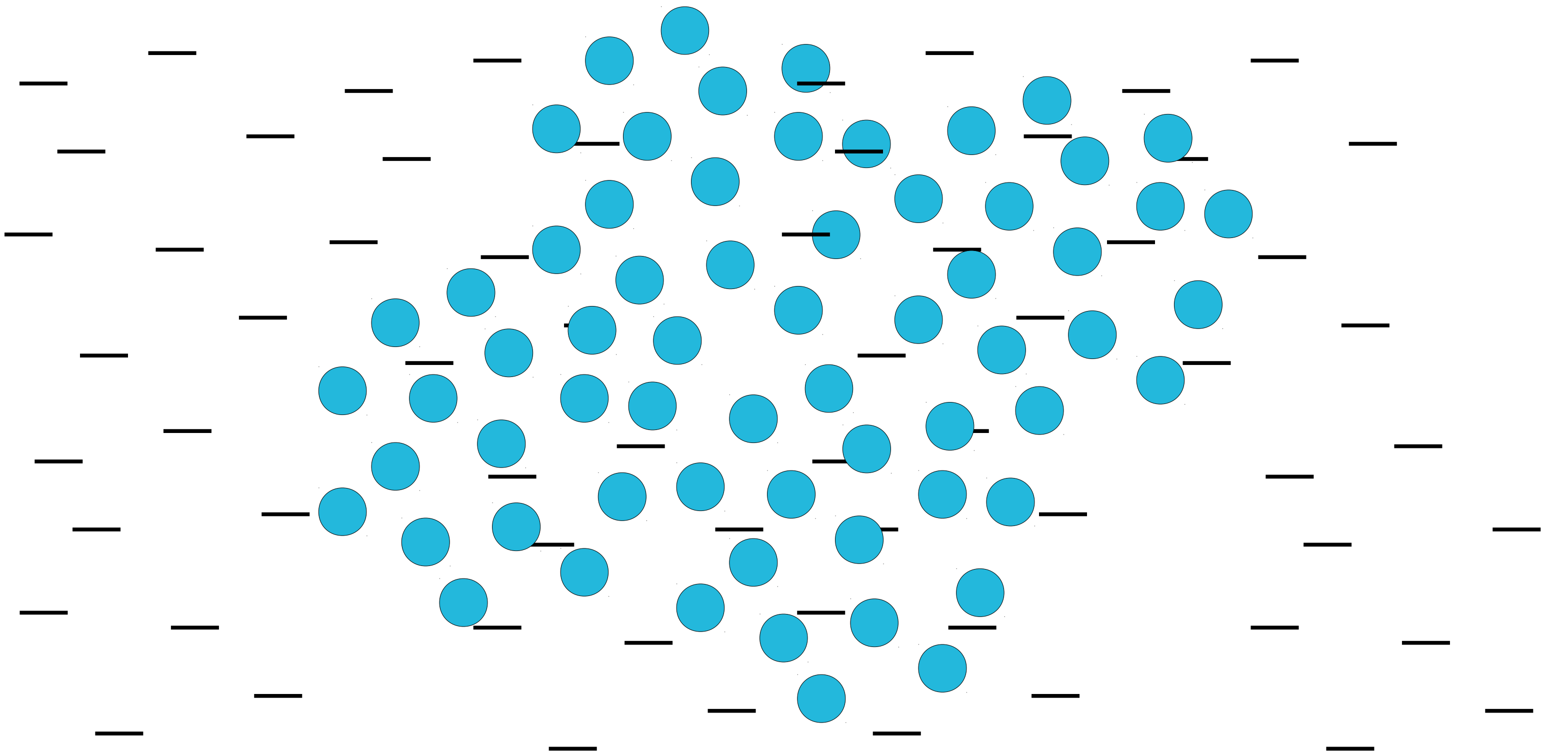
Hydrodynamic interactions - Smoluchowski





$$\mathbf{f}_1 = \Big(M(1) + M(1)GM(2) + M(1)GM(2)GM(1) + M(1)GM(2)GM(1)GM(2) + \ldots \Big)\mathbf{v}_0$$

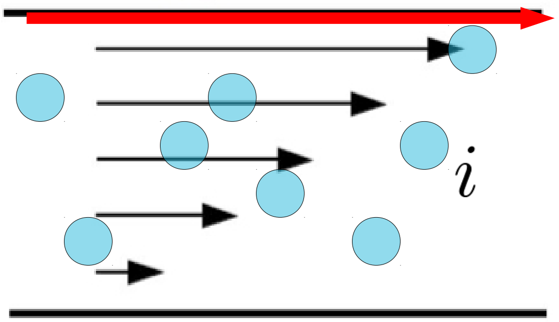
Hydrodynamic interactions are long-range



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

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

Beyond diluted suspensions



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

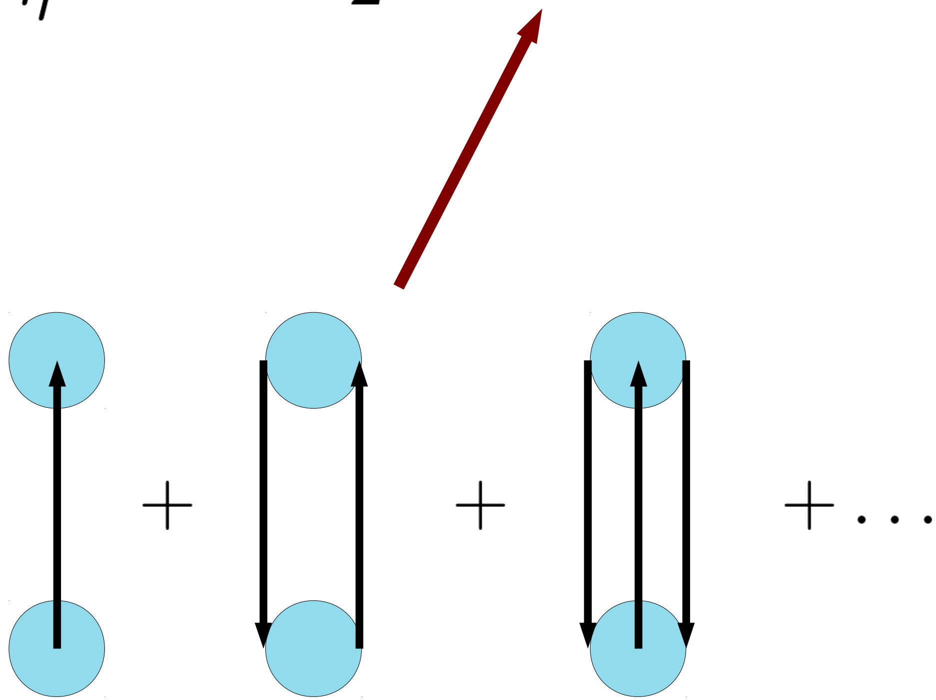
Saito:

$$\sum_{j\neq i}\mathbf{f}_j \rightarrow \int_{|\mathbf{R}-\mathbf{R}_i|>2a} d^3R\; n\; \langle\mathbf{f}\rangle$$

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

Two-particle hydrodynamic interactions

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



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

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

(ad hoc)

1982 – problem of long-range HI solved

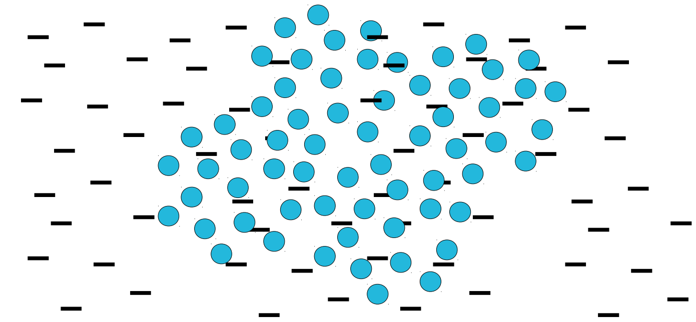
B. U. Felderhof,[1] G. W. Ford,[2] and E. G. D. Cohen[3]

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

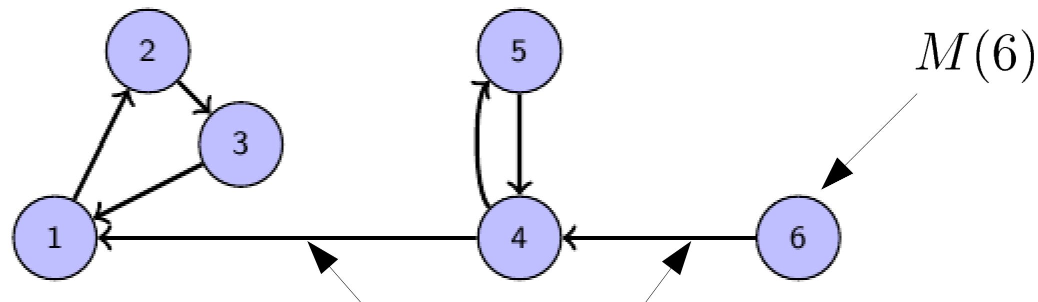
Effective viscosity - suspension in a flow

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



Example of scattering sequence (many-body):

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



short range hydrodynamic interactions
(strong interactions of close particles)

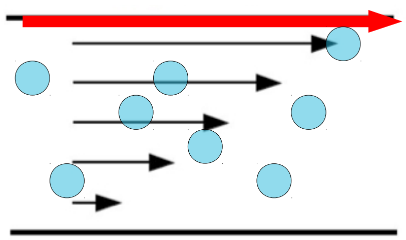
long range hydrodynamic interactions

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

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

Response of suspension

(effective viscosity)



$$\langle f \rangle = T^{irr} \langle v \rangle$$

average velocity field of suspension

average surface force

response operator

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

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)

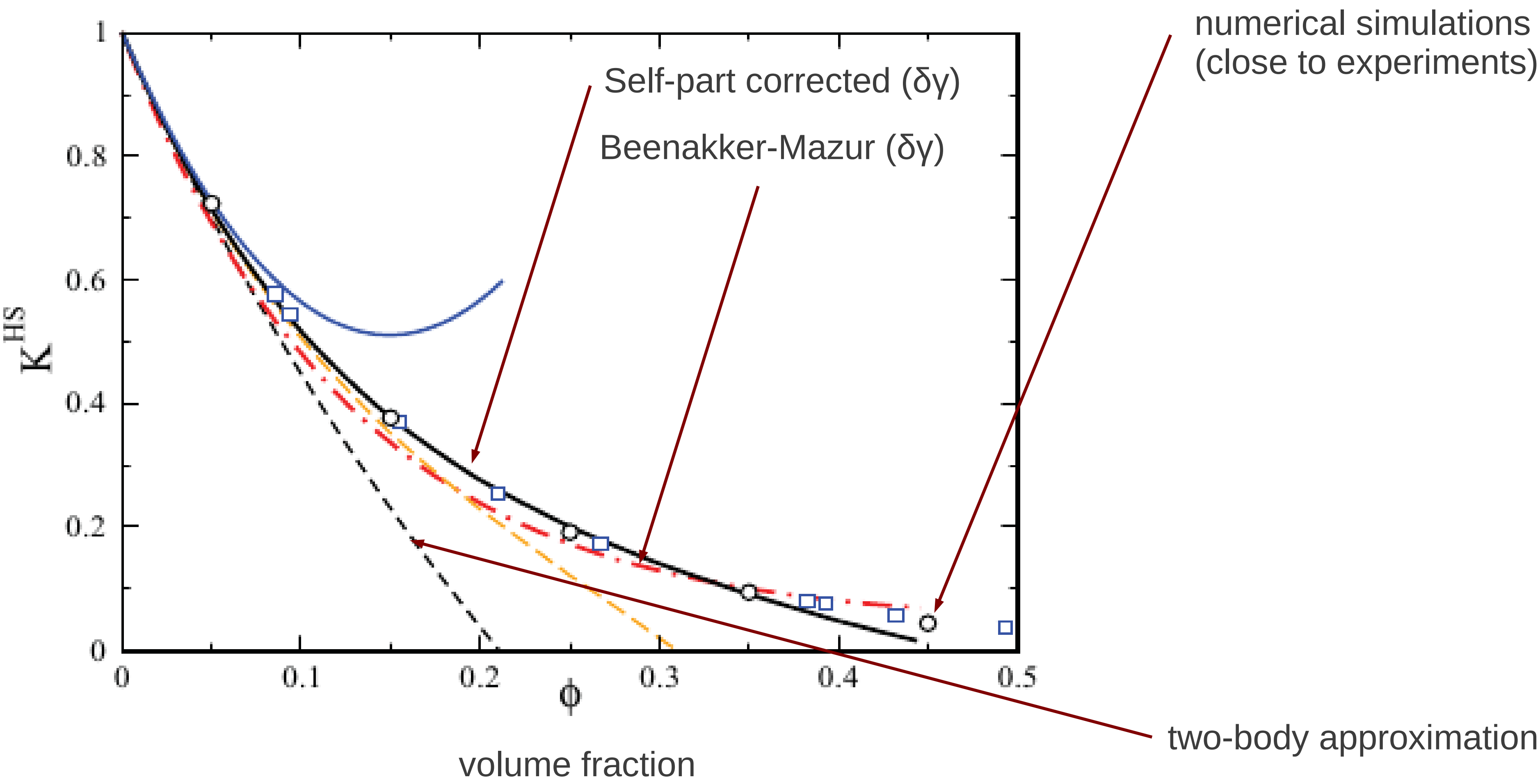
Oseen tensor (pure liquid):

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

Hydrodynamic interactions

Many-body character

Sedimentation coefficient for hard spheres

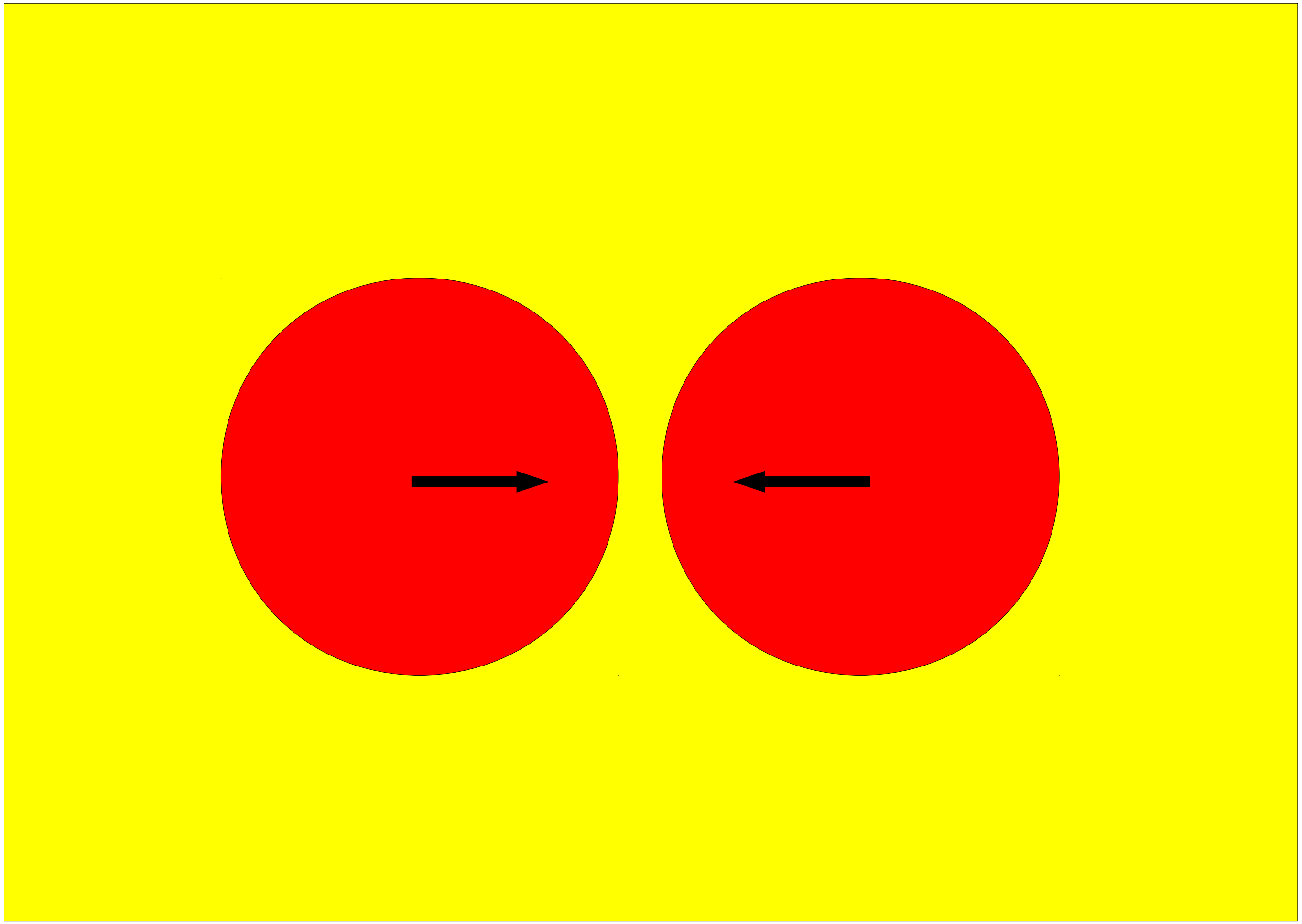


two-body approximation relevant for volume fractions less than about 5%

Hydrodynamic interactions

Strong interactions of close particles

For constant velocities asymptotically infinite drag force



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):

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

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

Effective propagator:

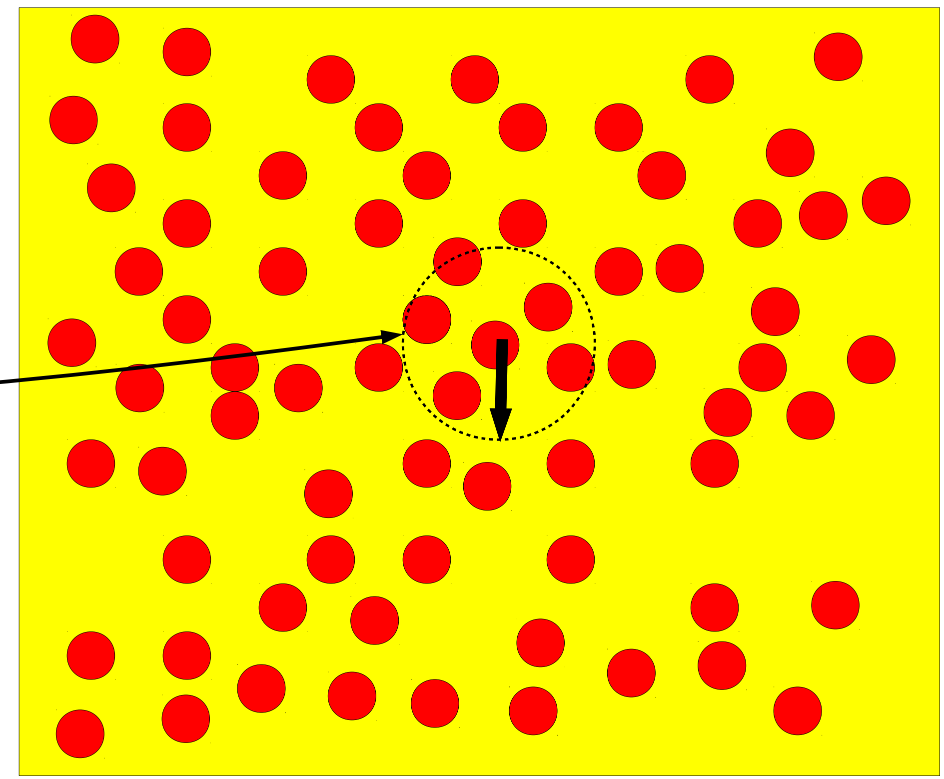
$$\mathbf{G}_{\text{eff}}(\mathbf{r}) \sim \frac{\eta}{\eta_{\text{eff}}} \mathbf{G}(\mathbf{r})$$

Effective Green function

Flow caused by force acting on particles in the area

total force acting on particles in the area

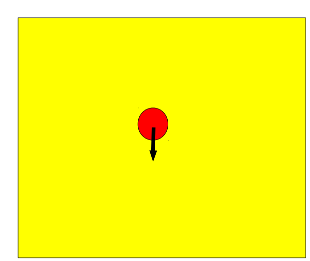
$$\mathbf{v}\left(\mathbf{r}\right) \sim \mathbf{G}_{\mathrm{eff}}\left(\mathbf{r}\right)\mathbf{F}$$



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



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

Two approximation schemes

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

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

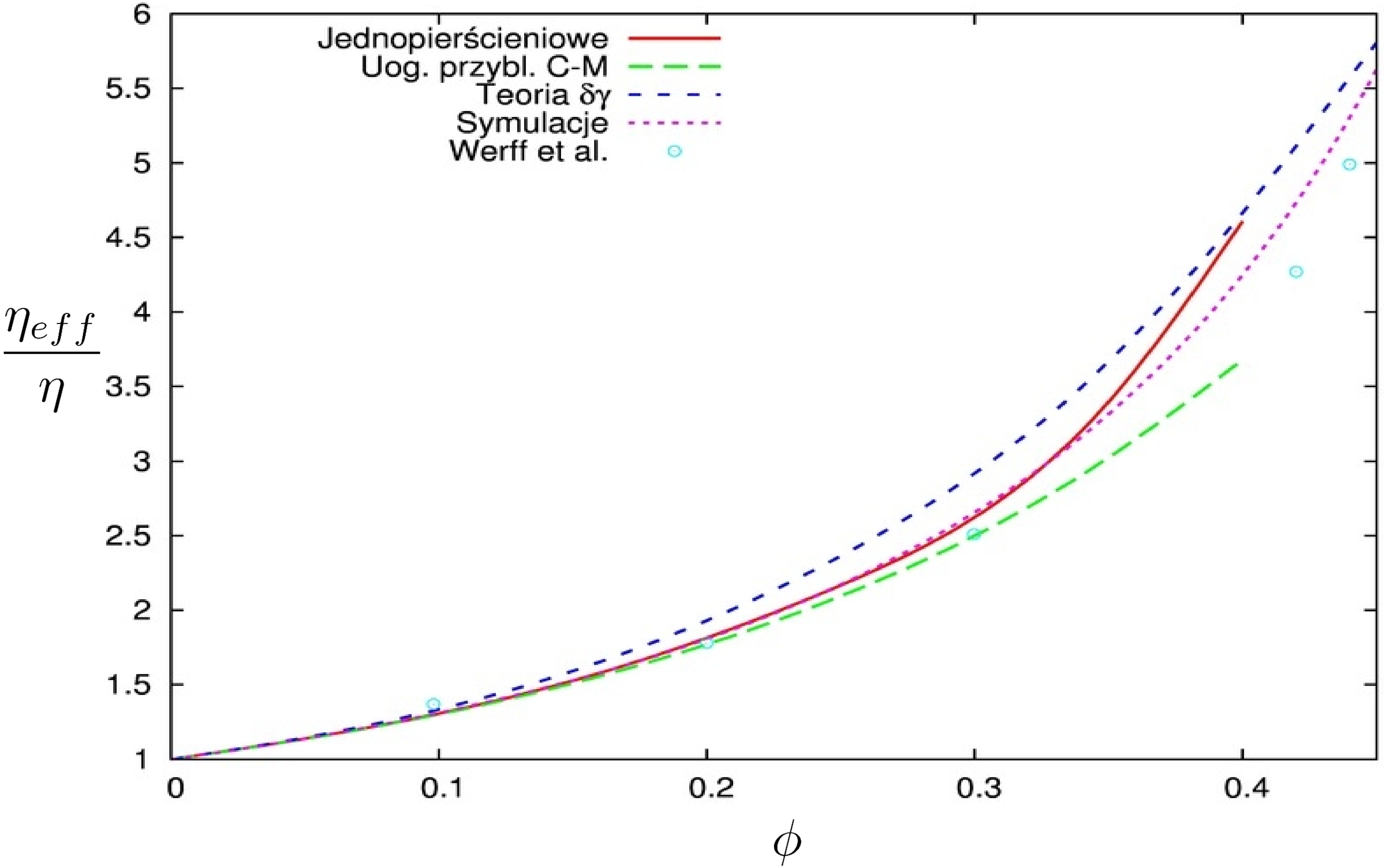
Clausius-Mossotti approximation $\Longrightarrow$ Generalized Clausius-Mossotti approximation

(two-body hydrodynamic interactions incomplete – the same as in δγ scheme (1983))

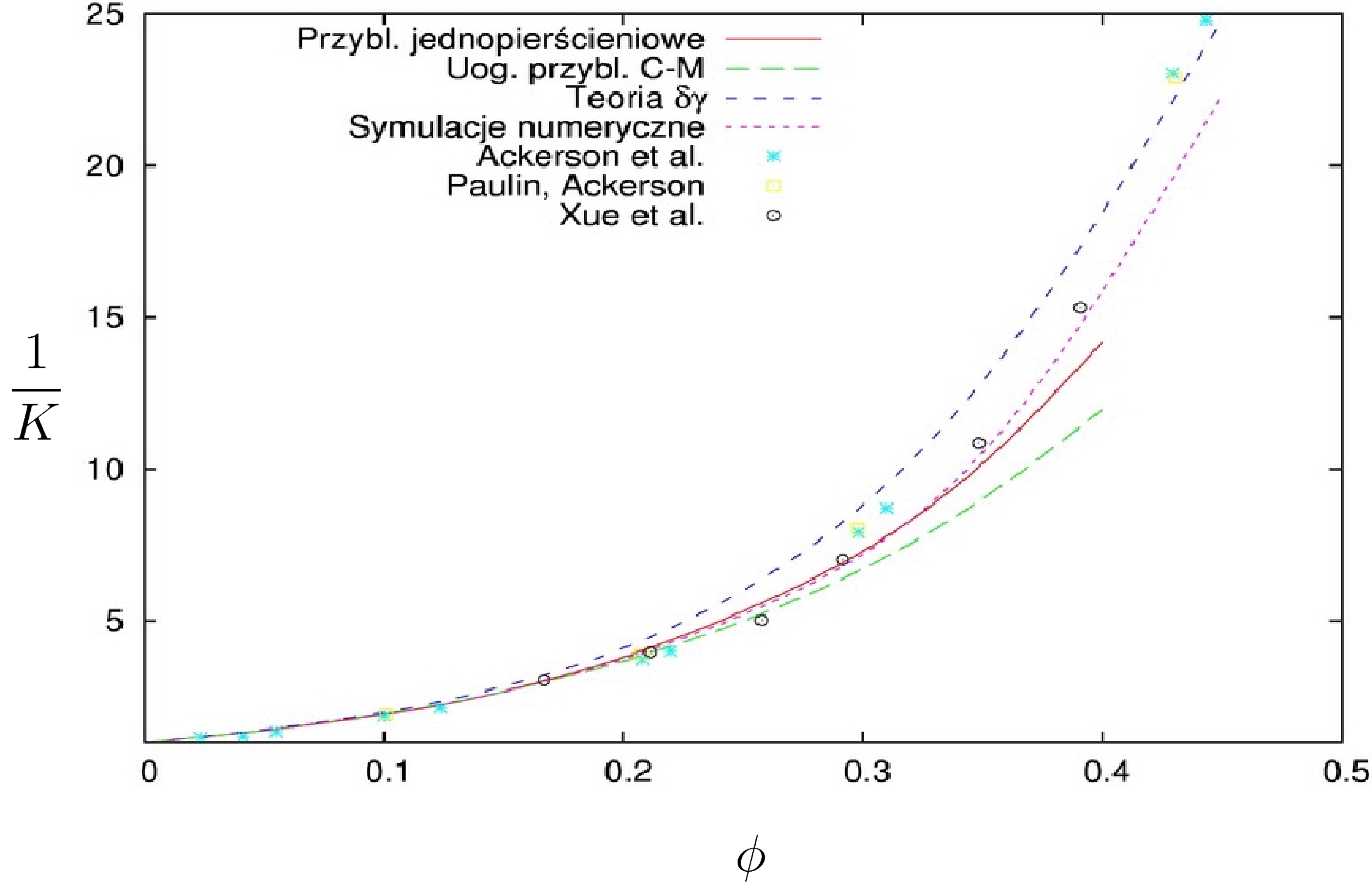
One-ring approximation (fully takes into account two-body hydrodynamic interactions)

Input:
-volume fraction
-two-body correlation function (PY); (three-particle correlation function by two body correlation function (Kirkwood))
-two-body hydrodynamic interactions

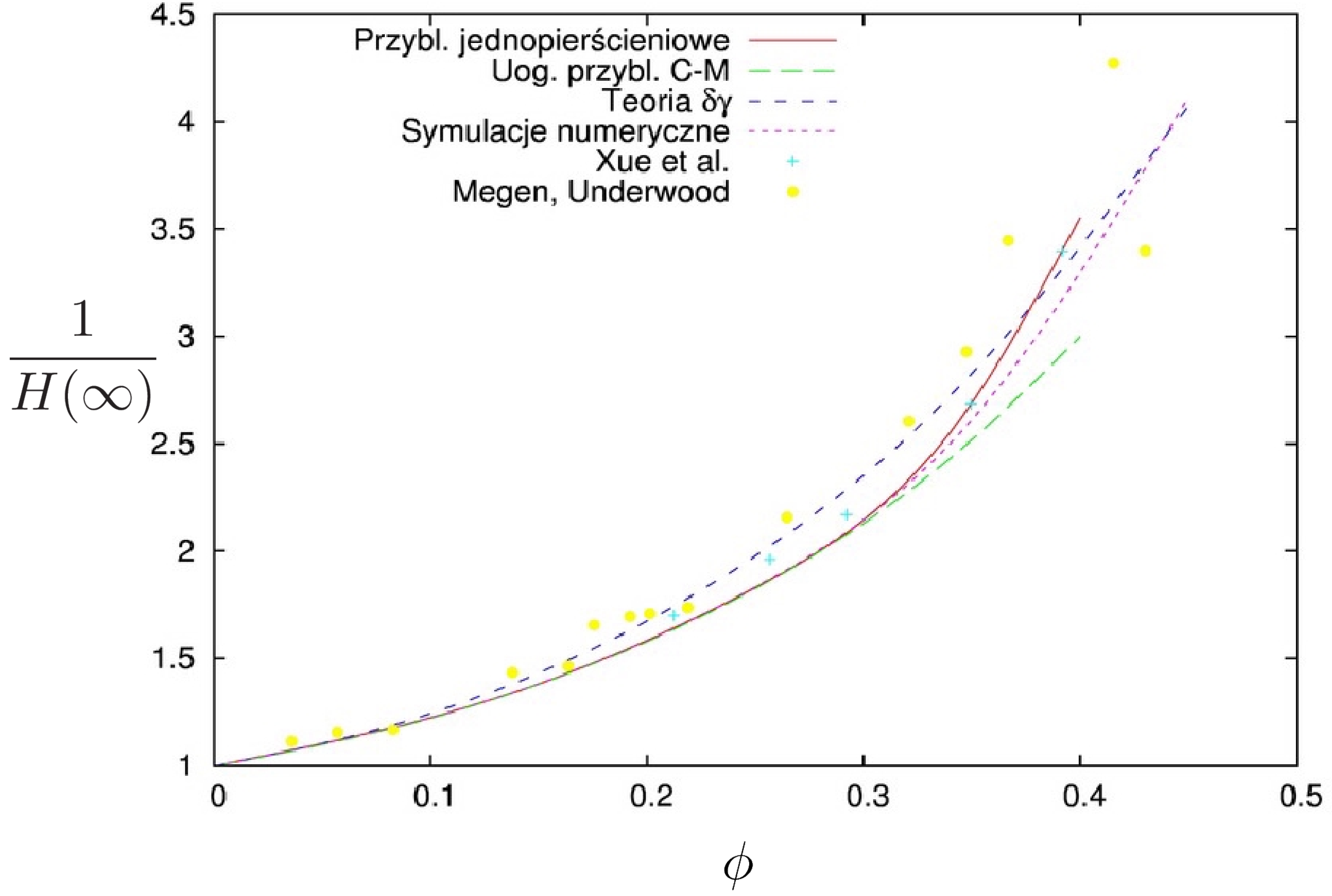
Effective viscosity



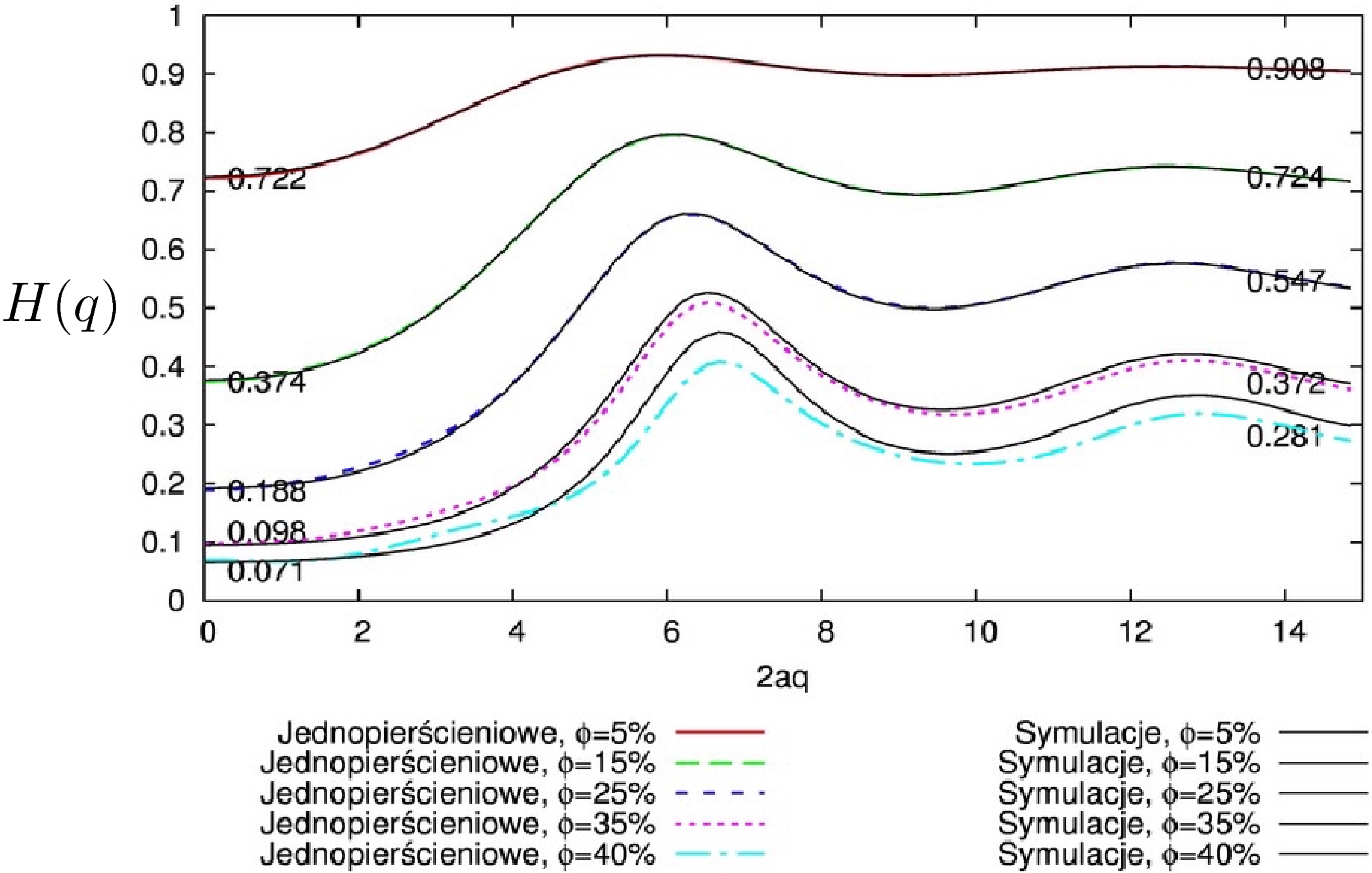
Sedimentation coefficient $K = H(0)$



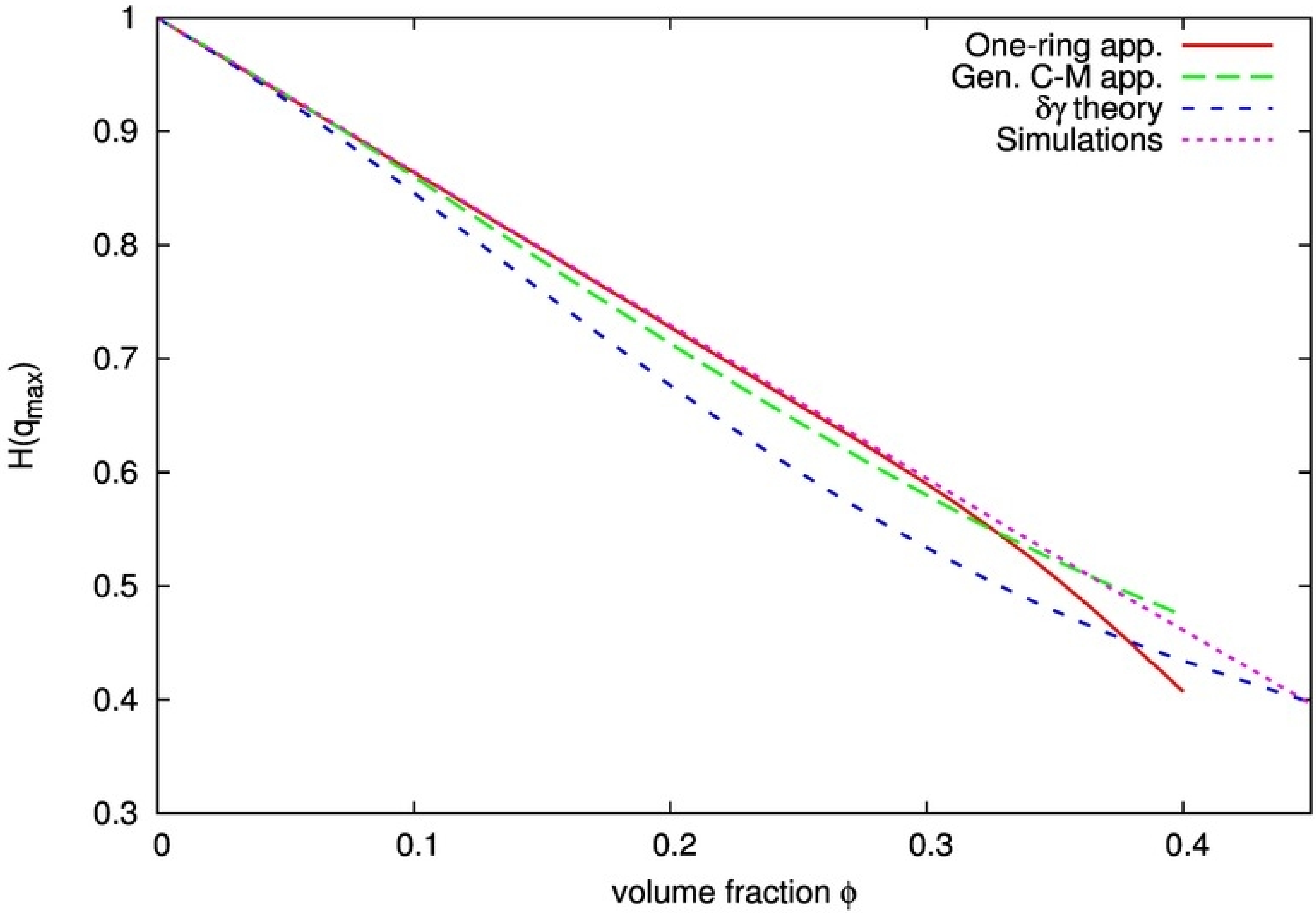
Inverse of mobility of single particle in suspension $H(\infty)$



Hydrodynamic factor – one ring approximation



Hydrodynamic function $H(q_{\mathrm{max}})$



Summary

- Long-range, many-body hydrodynamic interactions and strong interactions of close particles are important in suspensions
- Ring expansion for transport coefficients – can grasp all of three above features
- Two approximation schemes for transport coefficients:
  - generalized Clausius-Mossotti approximation (two-body hydrodynamic interactions not fully taken; comparable to $\delta\gamma$ scheme),
  - 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%)
- Simple generalization for different suspensions of spherical particles (droplets, spherical polymers) with different distributions (charged particles)

Powtarzające struktury T^{irr}

$$T^{irr} = T^{irr}_{CM}\left(1 - [hG]\,T^{irr}_{CM}\right)^{-1}$$

Operator Clausiusa-Mossottiego

Przybliżenie Clausiusa-Mossottiego: $T^{irr}_{CM} \approx nM$

$$T^{irr} = T^{irr}_{RCM}\left(1 - [hG_{\mathrm{eff}}]\,T^{irr}_{RCM}\right)^{-1}$$

Zrenormalizowany operator Clausiusa-Mossottiego

Uogólnione przybliżenie Clausiusa-Mossottiego: $T^{irr}_{RCM} \approx nB$

Metoda przybliżona: w oparciu o przybliżone równanie na T^{irr}_{RCM}

Zrenormalizowany operator Clausiusa-Mossottiego

$$
\begin{aligned}
T_{RCM}^{irr} &= \sum_{r=0}^{\infty} T_{RCM,r}^{irr}, \\
T_{RCM,0}^{irr}\left(\mathbf{R},\mathbf{R}'\right) &= \sum_{C_1} \int dC_1 n\left(C_1\right) S_I(C_1;\mathbf{R},\mathbf{R}'), \\
T_{RCM,1}^{irr}\left(\mathbf{R},\mathbf{R}'\right) &= \sum_{C_1,C_2} \int dC_1 dC_2 \int d^3\mathbf{R}_1 d^3\mathbf{R}_2 \; \left[H\left(C_1|C_2\right) - h\left(\mathbf{R}_1,\mathbf{R}_2\right)\right] \times \\
&\times n\left(C_1\right) S_I(C_1;\mathbf{R},\mathbf{R}_1) G_{eff}\left(\mathbf{R}_1,\mathbf{R}_2\right) n\left(C_2\right) S_I(C_2;\mathbf{R}_2,\mathbf{R}'), \\
&\ldots
\end{aligned}
$$

Przybliżenie jednopierścieniowe

Conajwyżej jeden pierścień w T_{RCM}^{irr}

Conajwyżej dwuciałowe oddziaływania w S_I

Przybliżenie Kirkwooda na trójciałową funkcję korelacji:

$$n\left(123\right) \approx n^3 g\left(12\right) g\left(13\right) g\left(23\right)$$

Renormalizcja oddziaływań dwuciałowych:

$$S_I(12) -> B S_I(12) B \qquad\qquad T^{irr} = nB + B\mathcal{T}^{irr}B$$

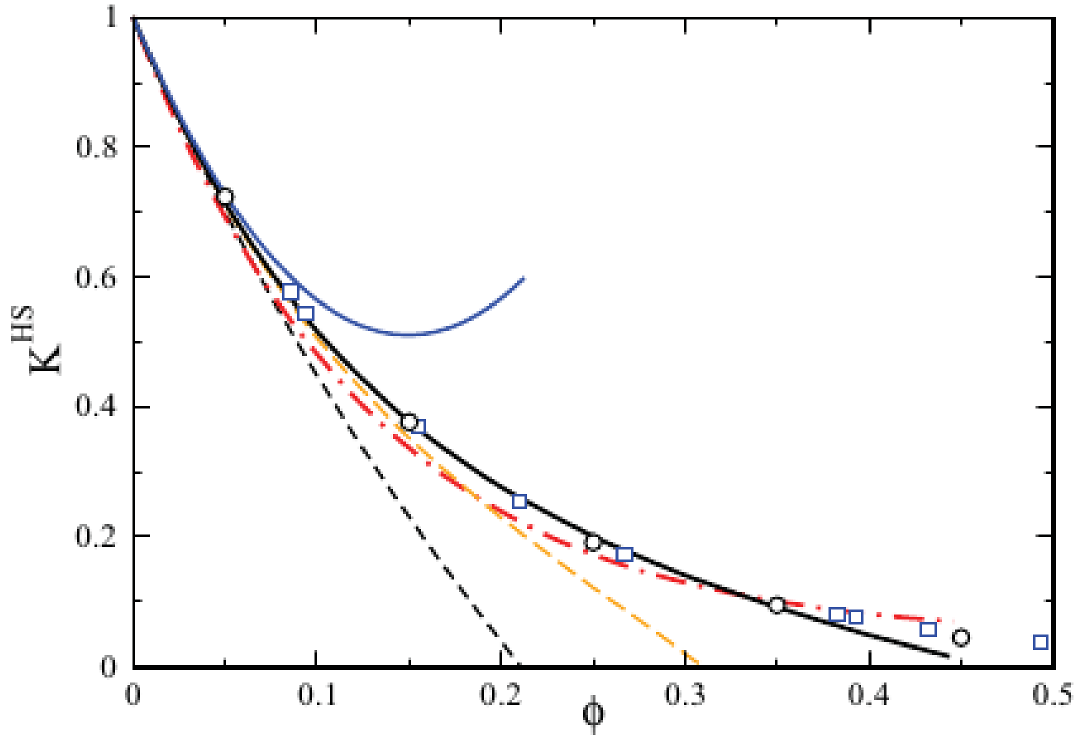


Fig. 6.3: *Reduced short-time sedimentation coefficient,* K^{HS}*, of neutral hard spheres. Open circles: Hydrodynamic force multipole simulation data by Abade et al. [26]. Open Squares: Lattice-Boltzmann simulation data by Segrè et al. [208]. Black dashed line: PA-scheme result. Dashed-dotted red line: uncorrected* $\delta\gamma$*-scheme result. Dashed orange line: self-part corrected* $\delta\gamma$*-scheme result, with* $d_s/d_{t,0}$ *taken from the PA-scheme. Solid black line: self-part corrected* $\delta\gamma$*-scheme result, with* $d_s/d_{t,0}$ *according to Eq. (4.26). Solid blue line: second-order virial result* $K^{HS} = 1 - 6.546\phi + 21.918\phi^2$ *[166]. The static structure factor input was obtained using the analytic Percus-Yevick solution.*