Micromechanics of Colloidal Suspensions: Dynamics of shear-induced aggregation

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Lagrangian transport: from complex flows to complex fluids

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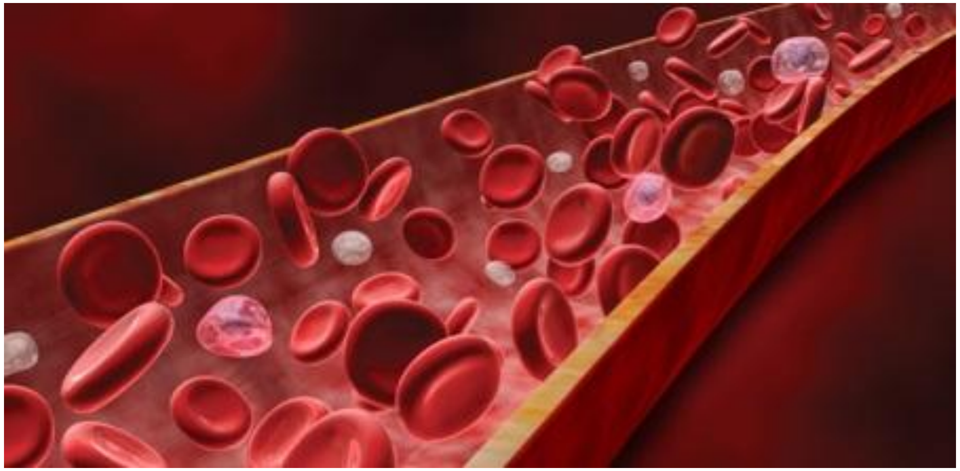
Fields of interest

- wet production of dispersed solids (ceramics, polymers, ...)
- environmental processes in aerosols/hydrosols
- compounding of plastics/elastomers
- food processing
- waste-water treatment
- rheology of suspensions

Complex fluids in daily life

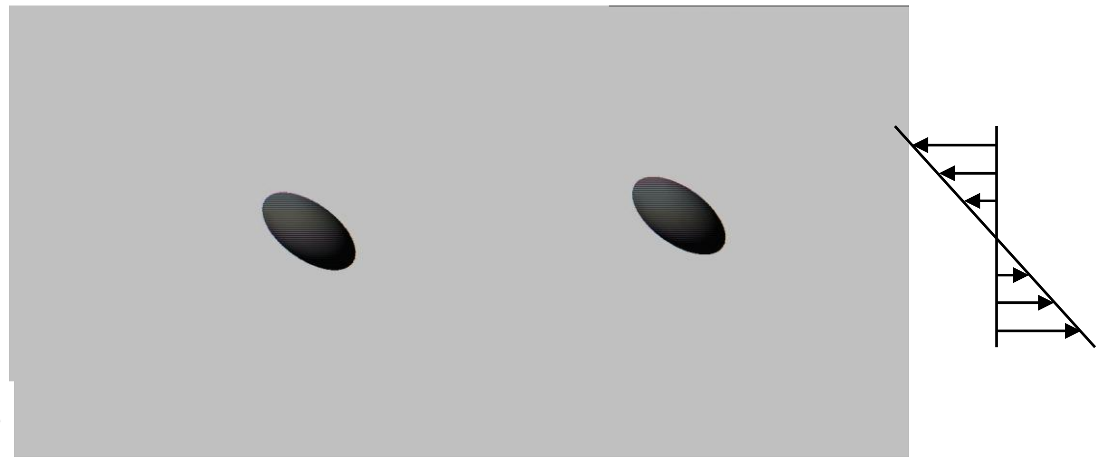






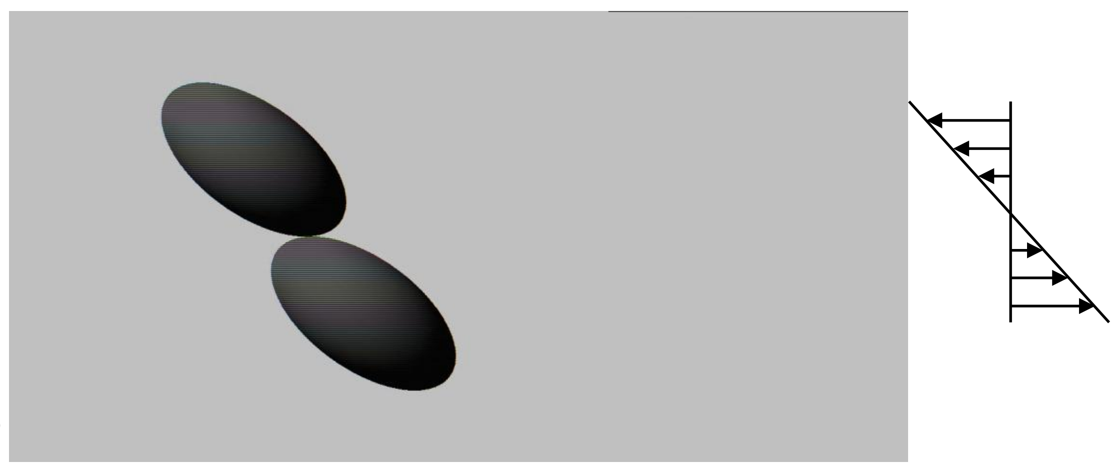
Role of the fluid flow

- Brings particles in close proximity, where attractive inter-particle forces become effective:
  Aggregation



$\dot{\gamma} = 50\ s^{-1}$

- Generates stresses on the formed aggregates that can exceed their cohesive strength:
  Breakup



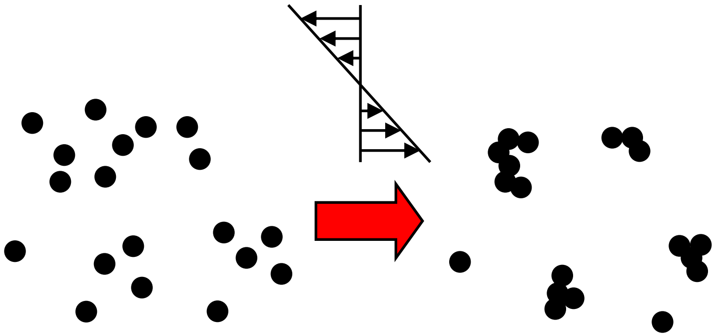
$\dot{\gamma} = 50000\ s^{-1}$

Aim and perspectives

Aim:
Development of a novel method to simulate the **dynamics of a dilute colloidal suspension** in simple flow fields through detailed modelling of colloidal and hydrodynamic interactions

Perspectives:
Predict kinetics of **agglomeration and breakup processes;**
Investigate the influence of physical properties and flow field on the structure of aggregates and on the response of the suspension

population initially made of monomers subject to homogeneous shear flow – negligible Brownian motion



Modelling approach

- The evolution of a population of colloidal particles in dilute systems is the result of many single aggregation and breakup events
- Single events are modelled by a **Discrete Element Method** (DEM) that takes into account hydrodynamic and adhesive forces in great detail.
- The sequence of events, for a representative sample of the population, is simulated statistically by a **Monte Carlo** reproduction of the global process.

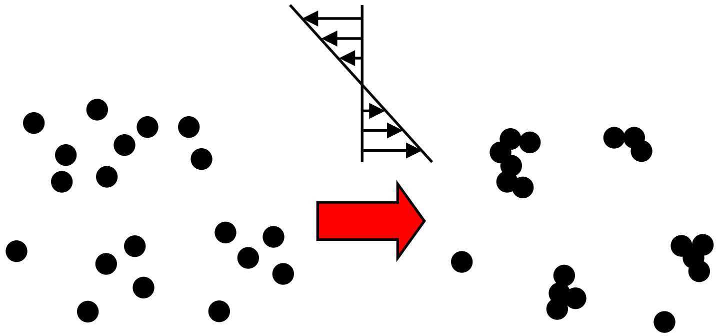
Summary:

- Contact forces / Colloidal interaction

- The simulation of single events:
  Discrete Element Method and Stokesian Dynamics

- The simulation of the process:
  Monte Carlo

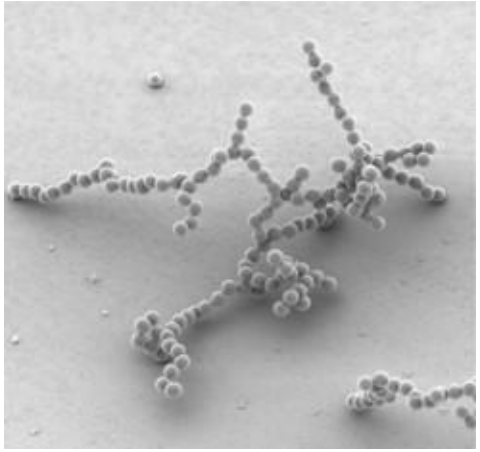
- Results and discussion



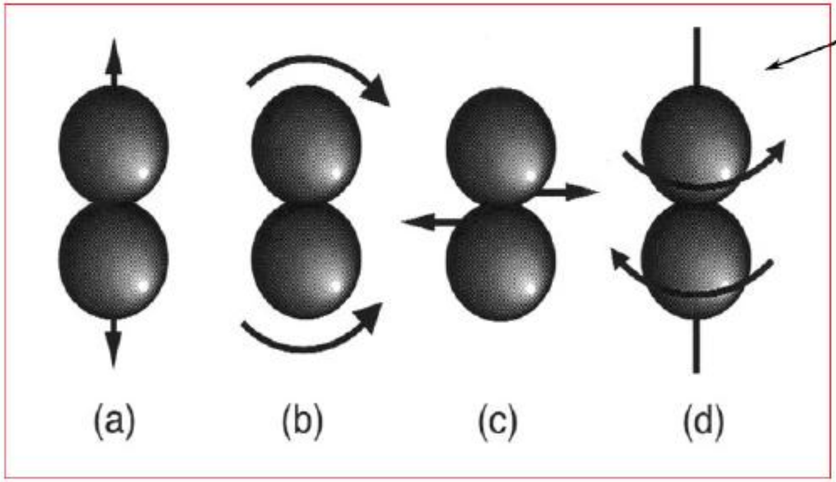
Contact Forces

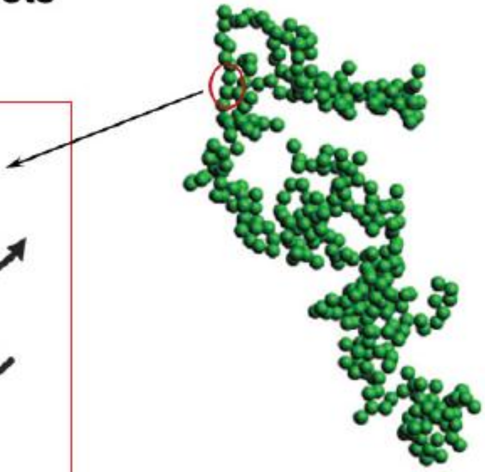
Aggregates

Structures held together by surface forces at intermonomer bonds



Degrees of freedom of interparticle contacts

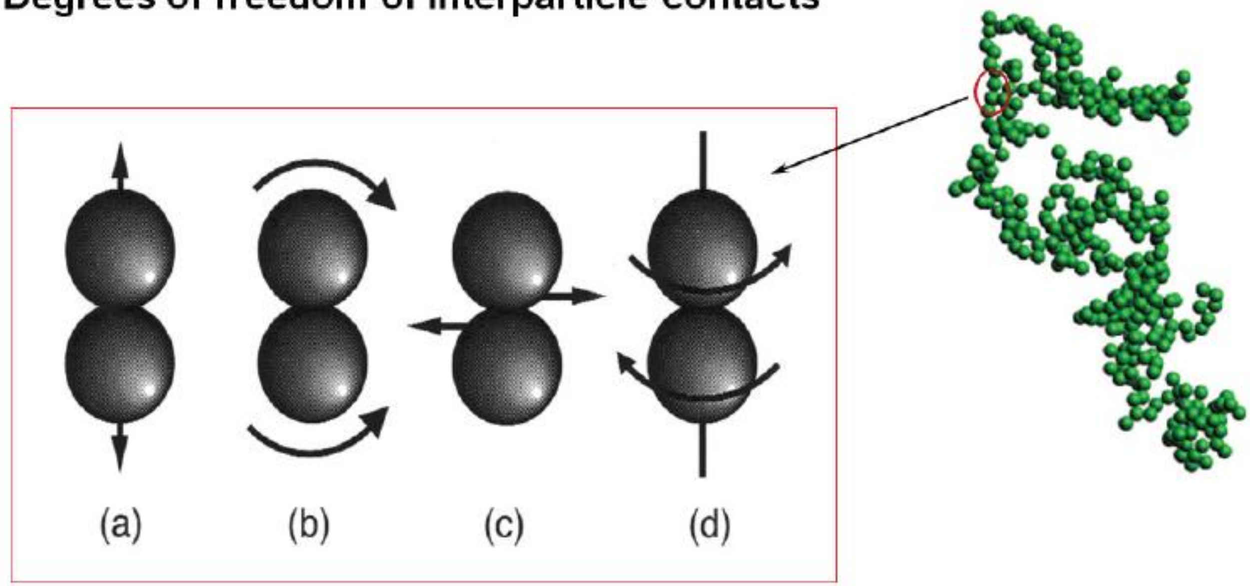




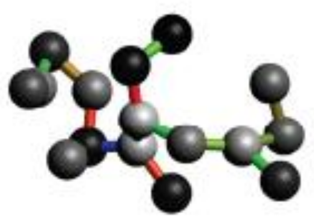
Aggregates

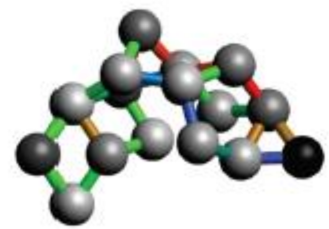
- Van der Waals attraction prevents detachment
- Deformation of contact area and surface friction may prevent sliding, rolling and twisting

Degrees of freedom of interparticle contacts



Aggregates



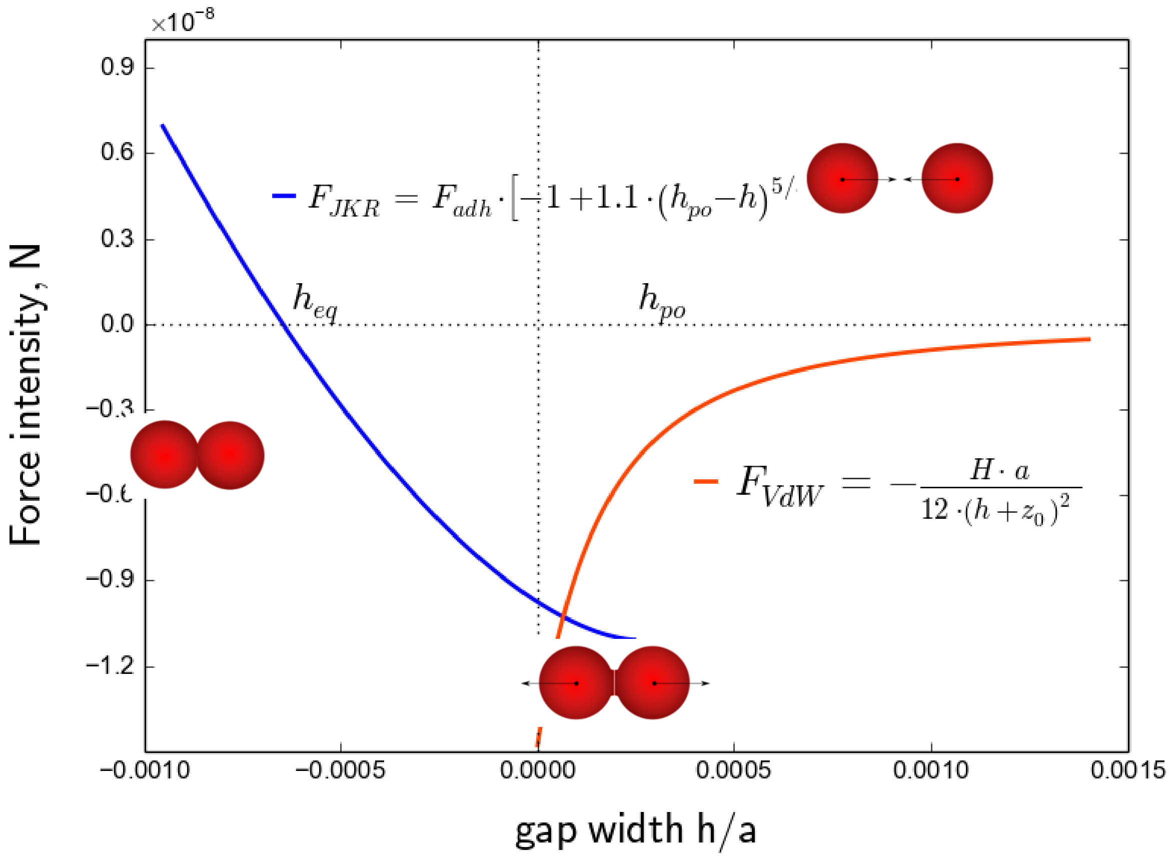


<u>Stiff aggregates</u>: fully rigid bonds, often low-density, with filaments of primary particles

<u>Soft aggregates</u>: may allow rotational/tangential motion at interparticle contacts (floppy contacts), usually highly compact

Normal degree of freedom

spherical primary particles



JKR theory of contact mechanics

Van der Waals attraction

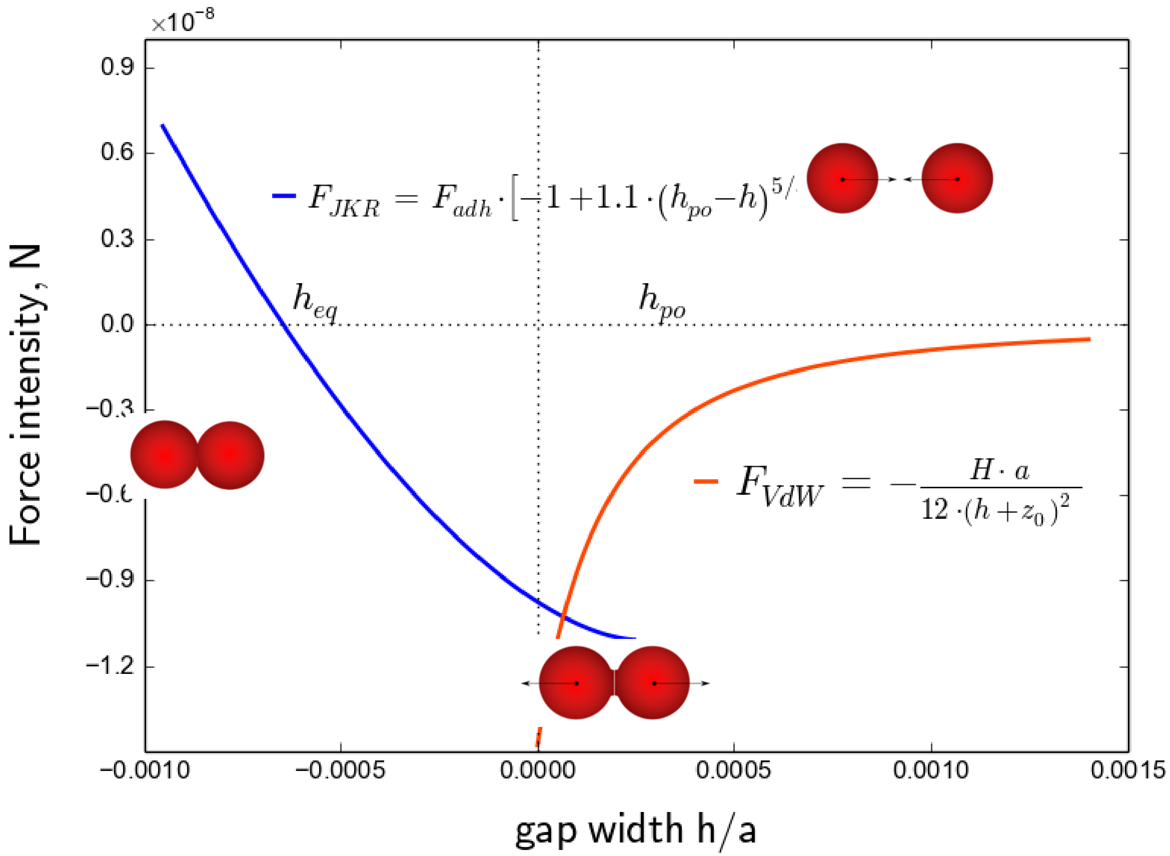
Colloidal particles, immersed in a liquid, interact via:

- Van der Waals interaction
- Elastic repulsion (after contact)
- Electrical double layer interaction
  Neglected (so far)

Contact – detachment hysteresis is assumed in the adhesive normal force, according to the JKR theory

Normal degree of freedom

spherical primary particles



JKR theory of contact mechanics

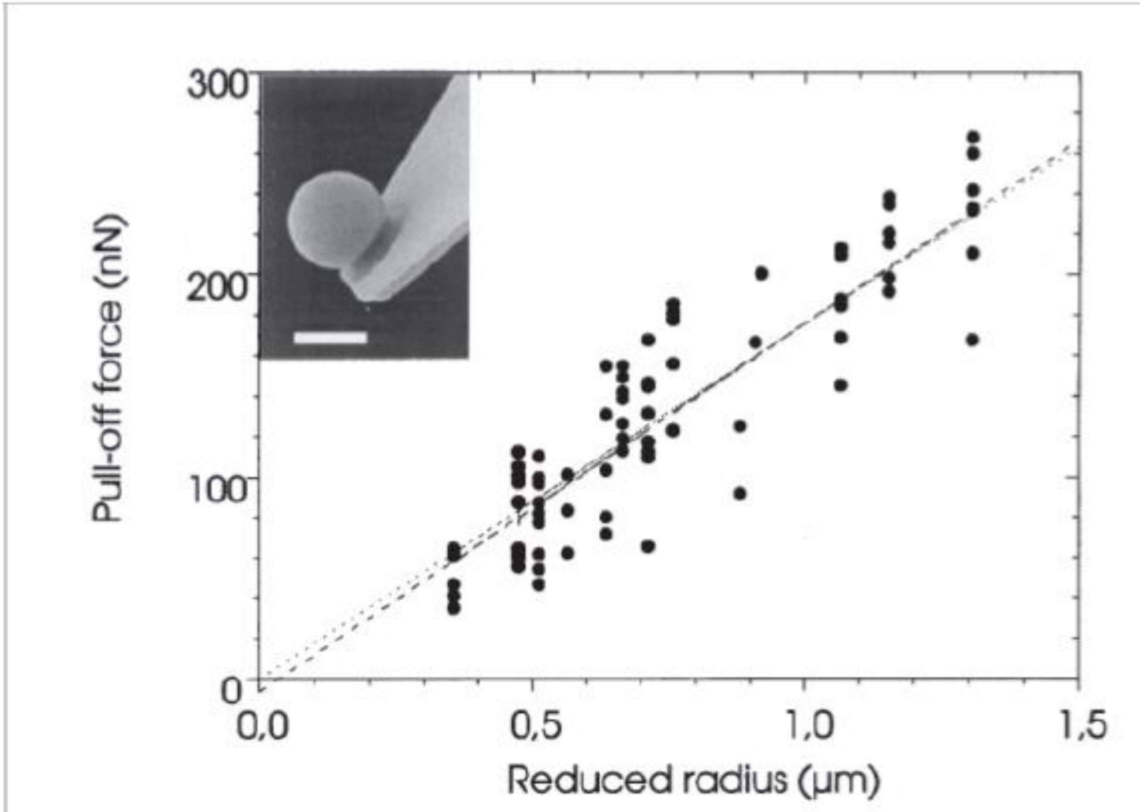
Van der Waals attraction

Polystyrene particles in a glycerol/water mixture

Temperature	298 K
Hamaker constant	$0.95 \cdot 10^{-20}$ J
Monomer radius	500 nm
Elastic modulus	3.4 GPa
Minimum approach distance	0.165 nm
Contact area radius	15 nm
Equilibrium dist.	0.32 nm
Pull-off distance	0.13 nm

Normal degree of freedom

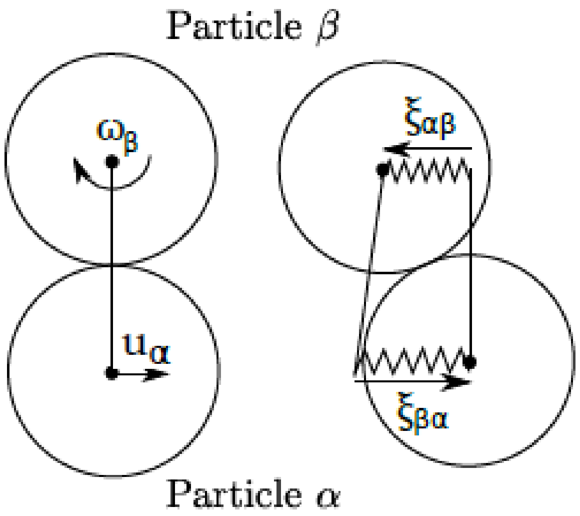
Large scatter of data with small particles
However, continuum models (like JKR) are valid



Heim, 1999

Tangential degrees of freedom

Model by Becker and Briesen (2012)
for elastic tangential deformations



Parameters:
spring stiffness
$k_t = 1.85 \cdot 10^{-5}$ N/m
maximum elastic elongation
$\xi_{max} = 50$ nm

Restoring forces and torques

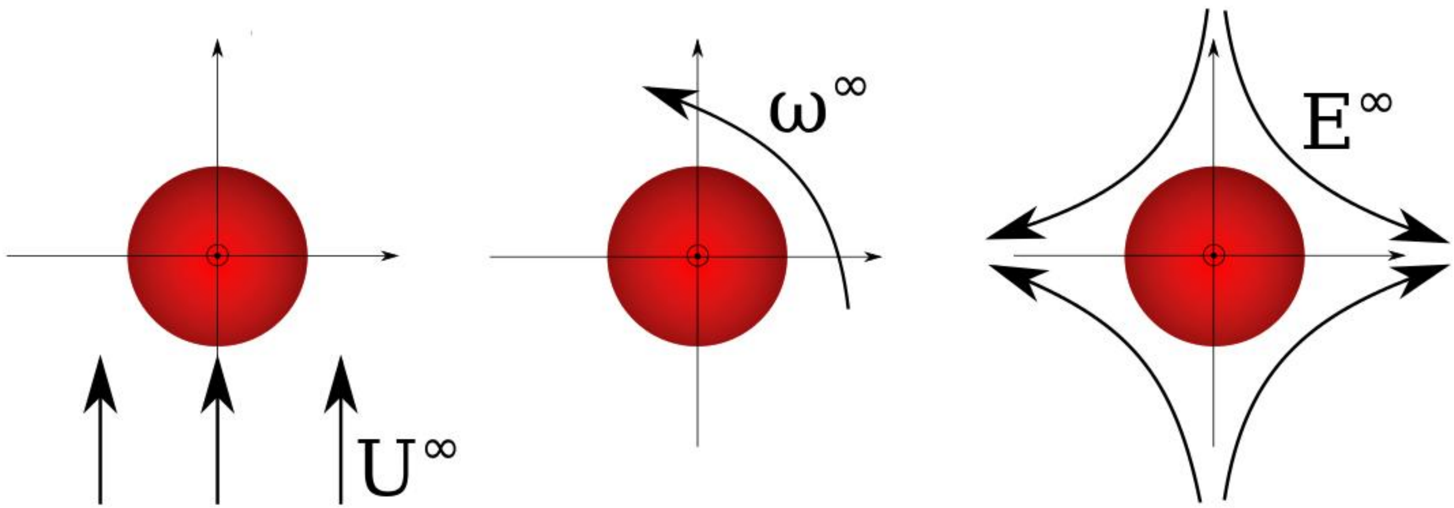
$$\mathbf{F}_\alpha = k_t\left(\boldsymbol{\xi}_{\alpha,\beta} - \boldsymbol{\xi}_{\beta,\alpha}\right) \qquad \mathbf{F}_\beta = k_t\left(\boldsymbol{\xi}_{\beta,\alpha} - \boldsymbol{\xi}_{\alpha,\beta}\right)$$

$$\mathbf{T}_\alpha = 2ak_t\mathbf{r}_{\alpha,\beta} \times \boldsymbol{\xi}_{\alpha,\beta} \qquad \mathbf{T}_\beta = -2ak_t\mathbf{r}_{\beta,\alpha} \times \boldsymbol{\xi}_{\beta,\alpha}$$

Simulation of Single Events

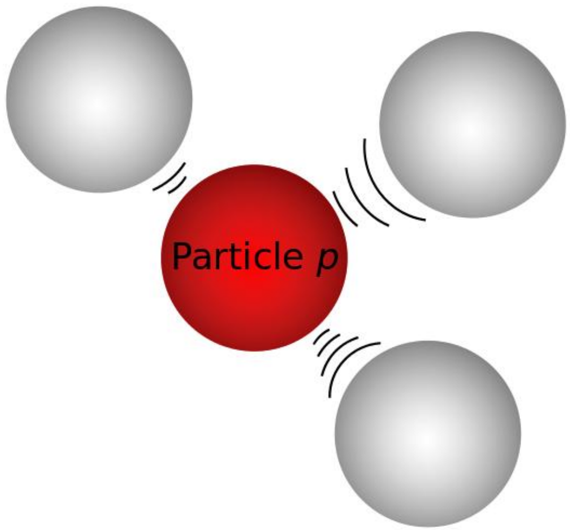
Hydrodynamic interaction – Isolated particle

In Stokes' regime the disturbance created by a single particle in a flow field can be seen as the superposition of the effects of a force, a torque and a stress tensor inducing a pure straining flow (stresslet)



$$\mathbf{F}_p^{\mathrm{H}} = 6\pi\eta a \left(\mathbf{u}^{\infty} - \mathbf{u}^{p}\right) \qquad \mathbf{T}_p^{\mathrm{H}} = 8\pi\eta a^{3} \left(\boldsymbol{\omega}^{\infty} - \boldsymbol{\omega}^{p}\right) \qquad \mathsf{S}_p^{\mathrm{H}} = \frac{20}{3}\pi\eta a^{3}\mathsf{E}^{\infty}$$

Stokesian dynamics: hydrodynamics of interacting particles



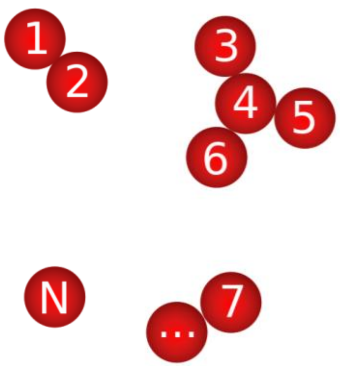
$$\mathbf{F}_p^{\mathrm{H}} = 6\pi\eta a \left(\mathbf{u}^{\infty} - \mathbf{u}^{p}\right) + \sum_{i \neq p} f^{F}\left(\mathbf{F}_i^{\mathrm{H}}, \mathbf{T}_i^{\mathrm{H}}, \mathsf{S}_i^{\mathrm{H}}\right)$$

$$\mathbf{T}_p^{\mathrm{H}} = 8\pi\eta a^{3} \left(\boldsymbol{\omega}^{\infty} - \boldsymbol{\omega}^{p}\right) + \sum_{i \neq p} f^{T}\left(\mathbf{F}_i^{\mathrm{H}}, \mathbf{T}_i^{\mathrm{H}}, \mathsf{S}_i^{\mathrm{H}}\right)$$

$$\mathsf{S}_p^{\mathrm{H}} = \frac{20}{3}\pi\eta a^{3}\mathsf{E}^{\infty} + \sum_{i \neq p} f^{S}\left(\mathbf{F}_i^{\mathrm{H}}, \mathbf{T}_i^{\mathrm{H}}, \mathsf{S}_i^{\mathrm{H}}\right)$$

Accurate predictions can be obtained by taking into account the far-field form of mutal interaction for all pairs of particles, except the closest one, where the lubrication interaction is considered.

Stokesian dynamics: hydrodynamics of interacting particles



N interacting particles

$$
\underbrace{\begin{Bmatrix} \mathbf{u}_1^{(p)} - \mathbf{u}^{\infty} \\ \vdots \\ \mathbf{u}_N^{(p)} - \mathbf{u}^{\infty} \end{Bmatrix}}_{\text{unknown}}
\begin{Bmatrix} \\ \\ \end{Bmatrix}
$$

$$
\left\{ \begin{matrix} \mathbf{u}_1^{(p)} - \mathbf{u}^{\infty} \\ \vdots \\ \mathbf{u}_N^{(p)} - \mathbf{u}^{\infty} \\ \boldsymbol{\omega}_1^{(p)} - \boldsymbol{\omega}^{\infty} \\ \vdots \\ \boldsymbol{\omega}_N^{(p)} - \boldsymbol{\omega}^{\infty} \\ -\mathrm{E}^{\infty} \\ \vdots \\ -\mathrm{E}^{\infty} \end{matrix} \right\} = -\frac{1}{\mu} [\mathcal{M}] \cdot \left\{ \begin{matrix} \mathbf{F}_1^{H} = -\mathbf{F}_1^{coll} \\ \vdots \\ \mathbf{F}_N^{H} = -\mathbf{F}_N^{coll} \\ \mathbf{T}_1^{H} = -\mathbf{T}_N^{coll} \\ \vdots \\ \mathbf{T}_N^{H} = -\mathbf{T}_1^{coll} \\ \mathbf{S}_1^{H} \\ \vdots \\ \mathbf{S}_N^{H} \end{matrix} \right\}
$$

unknown ($\mathbf{u}_1^{(p)} - \mathbf{u}^{\infty}$ … $\mathbf{u}_N^{(p)} - \mathbf{u}^{\infty}$)

unknown ($\boldsymbol{\omega}_1^{(p)} - \boldsymbol{\omega}^{\infty}$ … $\boldsymbol{\omega}_N^{(p)} - \boldsymbol{\omega}^{\infty}$)

known ($-\mathrm{E}^{\infty}$ … $-\mathrm{E}^{\infty}$)

known ($-\mathbf{F}^{coll}$, $-\mathbf{T}^{coll}$)

unknown ($\mathbf{S}_1^{H}$ … $\mathbf{S}_N^{H}$)

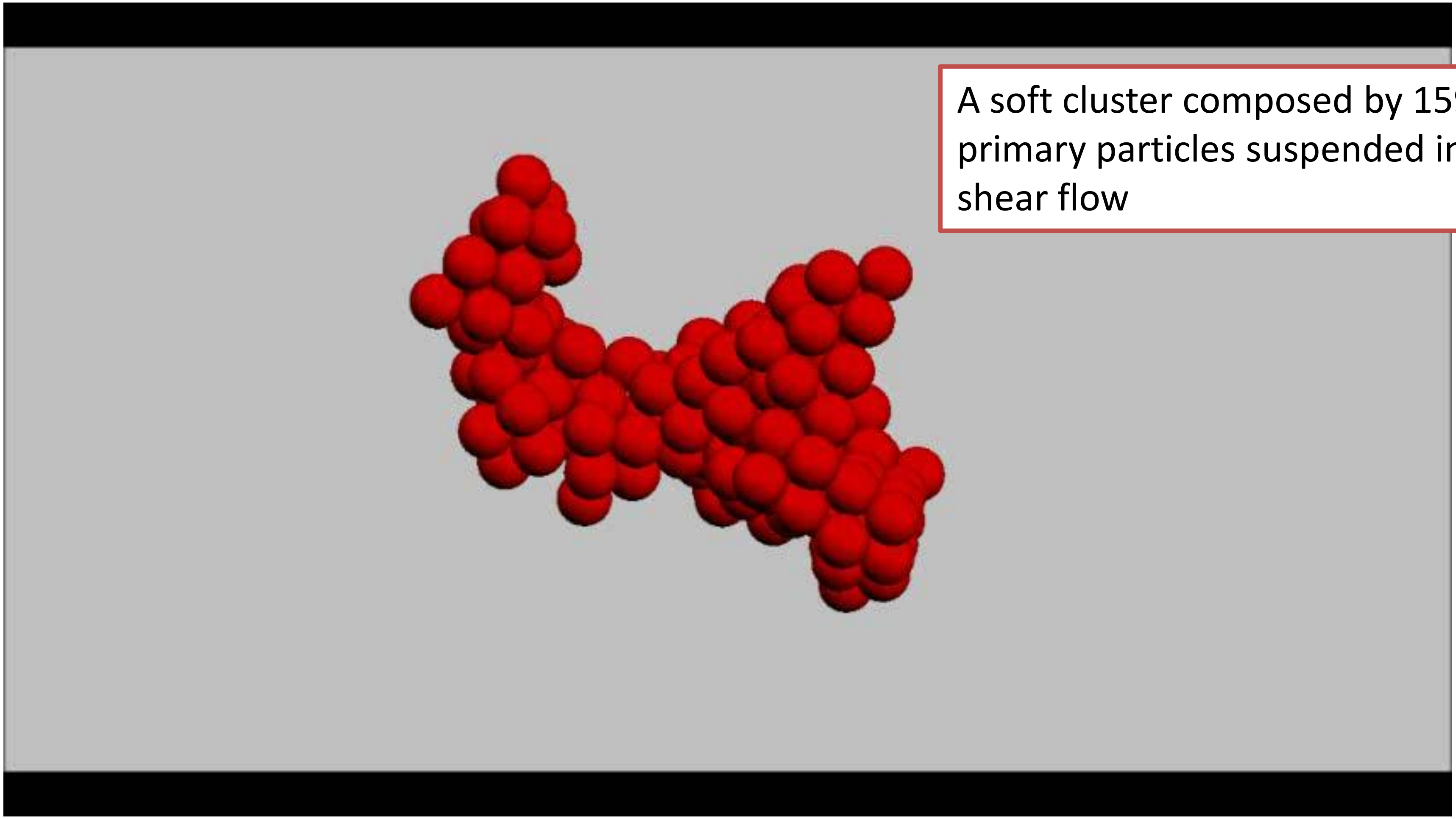
$[\mathcal{M}]$

Mobility matrix,
function of the
instantaneous geometry
Size: $11N$ x $11N$

Computational cost $\propto$ (Number of primary particles) ^{3}

Example of DEM-SD simulation

The integration of the equation of motion gives the trajectory of each primary particle



A soft cluster composed by 159 primary particles suspended in shear flow

Stokesian dynamics: hydrodynamics of interacting particles

Computational cost $\propto$ (Number of primary particles) ^{3}

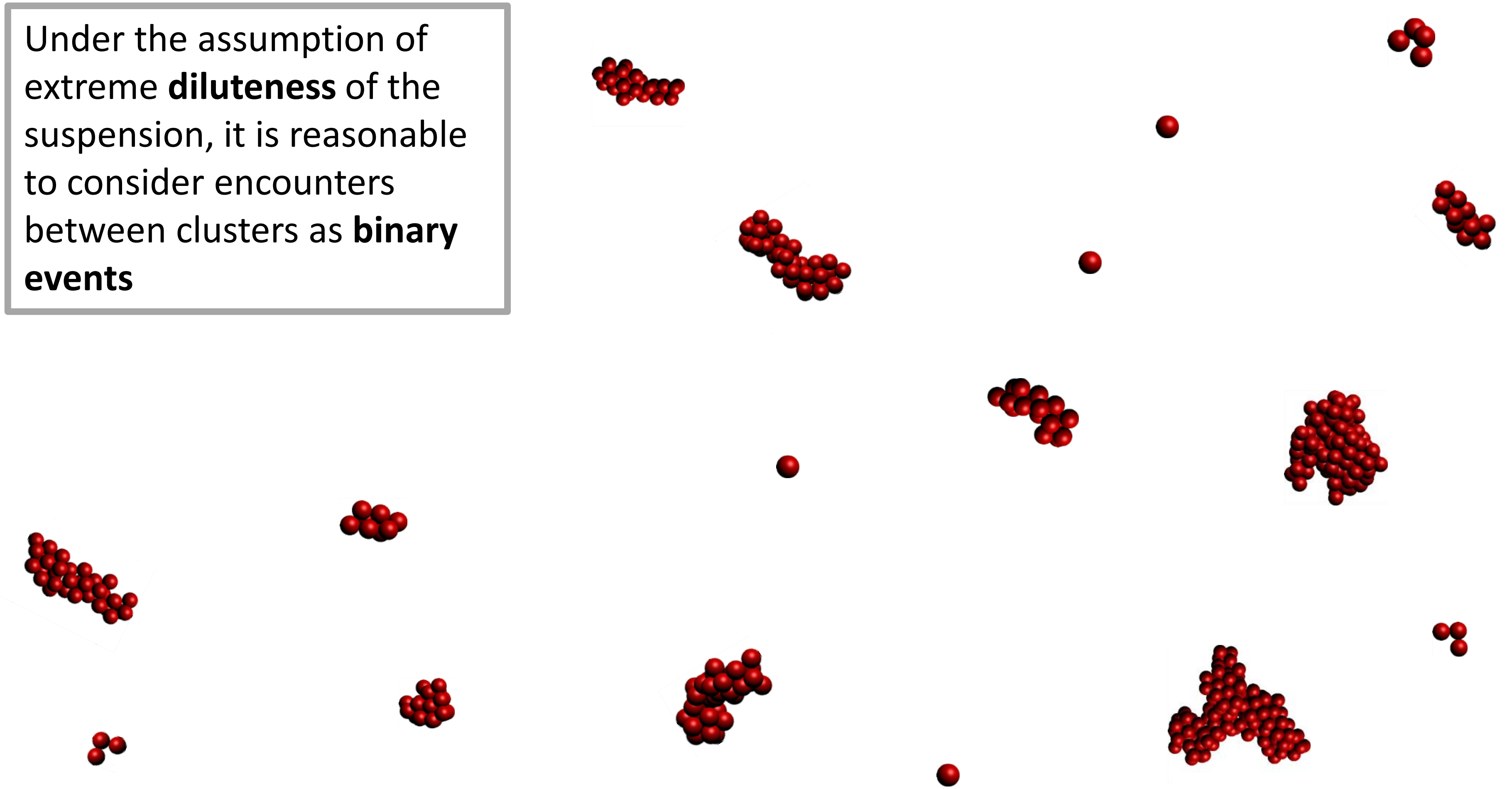
Calculation of particle motion requires calculation and inversion of the mobility matrix at every time step. The high computational effort restricts the applicability of the method to small populations of primary particles.

Consequence:
Only the hydrodynamics of single aggregates or pairs of aggregates can be simulated in reasonable time

Monte Carlo simulation of the process

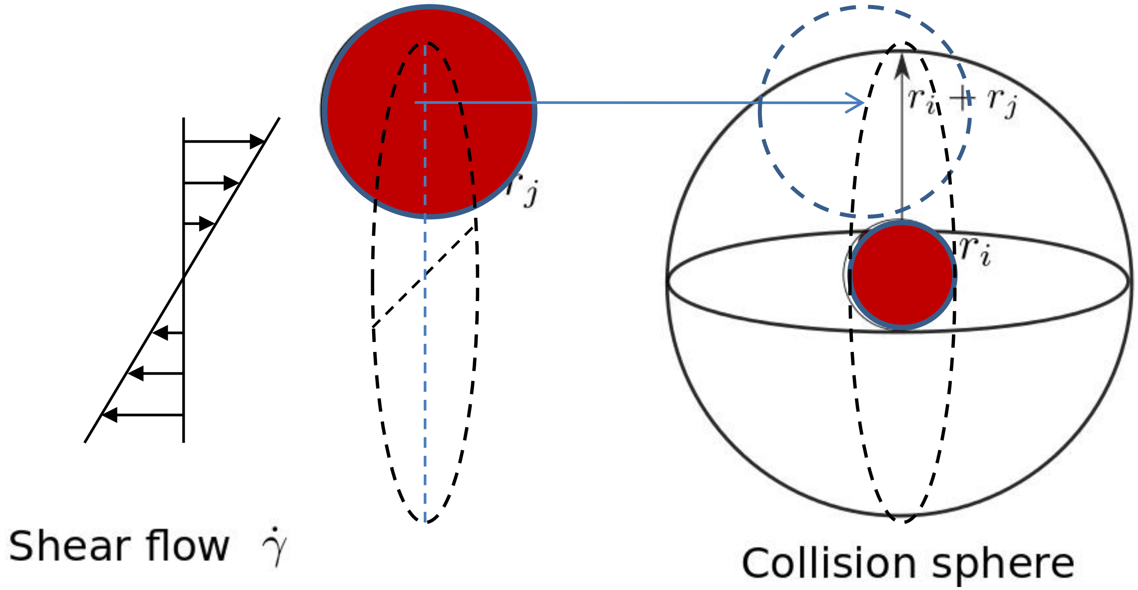
Monte Carlo simulation of shear-induced aggregation

Under the assumption of extreme **diluteness** of the suspension, it is reasonable to consider encounters between clusters as **binary events**



Monte Carlo method

- For a couple of spherical non-interacting particles the statistically expected frequency of encounters (=collisions) between aggregates in a shear flow is (Smoluchowski):
- $$f_{ij} = \frac{4}{3}(r_i + r_j)^3 \dot{\gamma}/V$$



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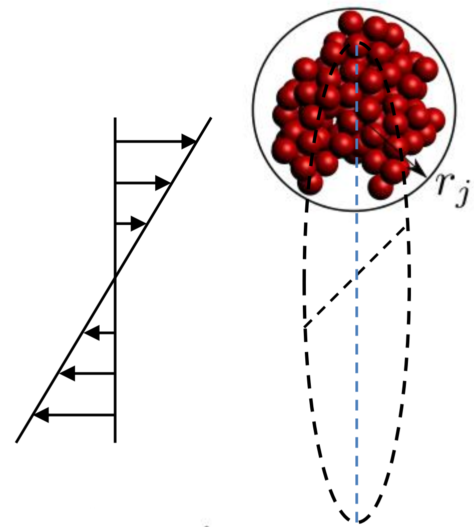
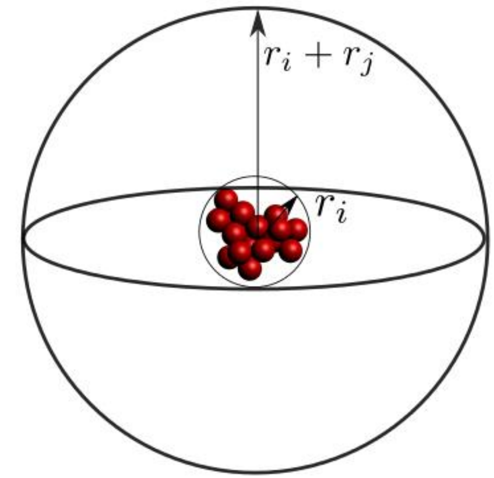


Shear flow $\dot{\gamma}$

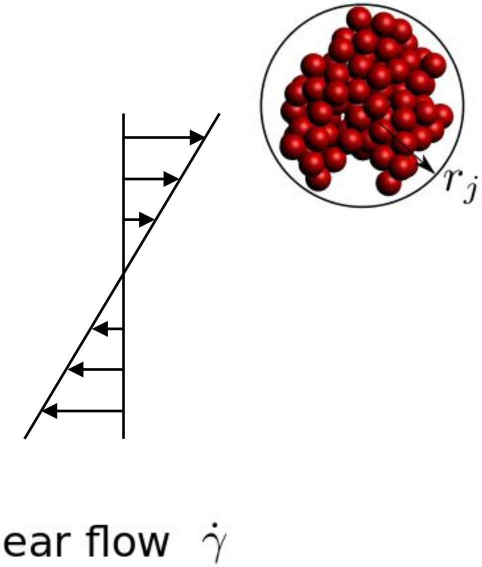


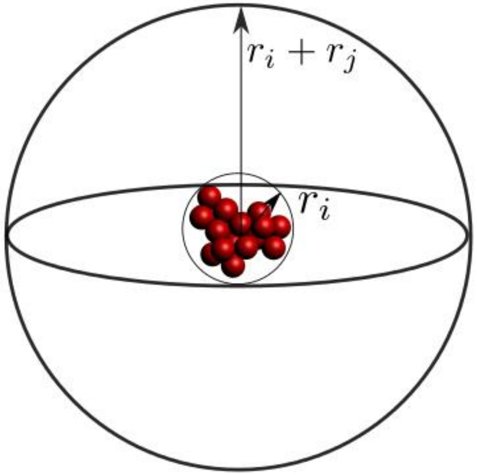
Collision sphere

- The same expression can be used to characterise encounters for aggregates as well, and **generate statistically a sequence of events** among all the aggregates of the population that reproduce a particular realization of the process.

- However, in this case , the outcome of an encounter is not necessarily a collision

Monte Carlo method



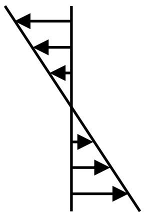


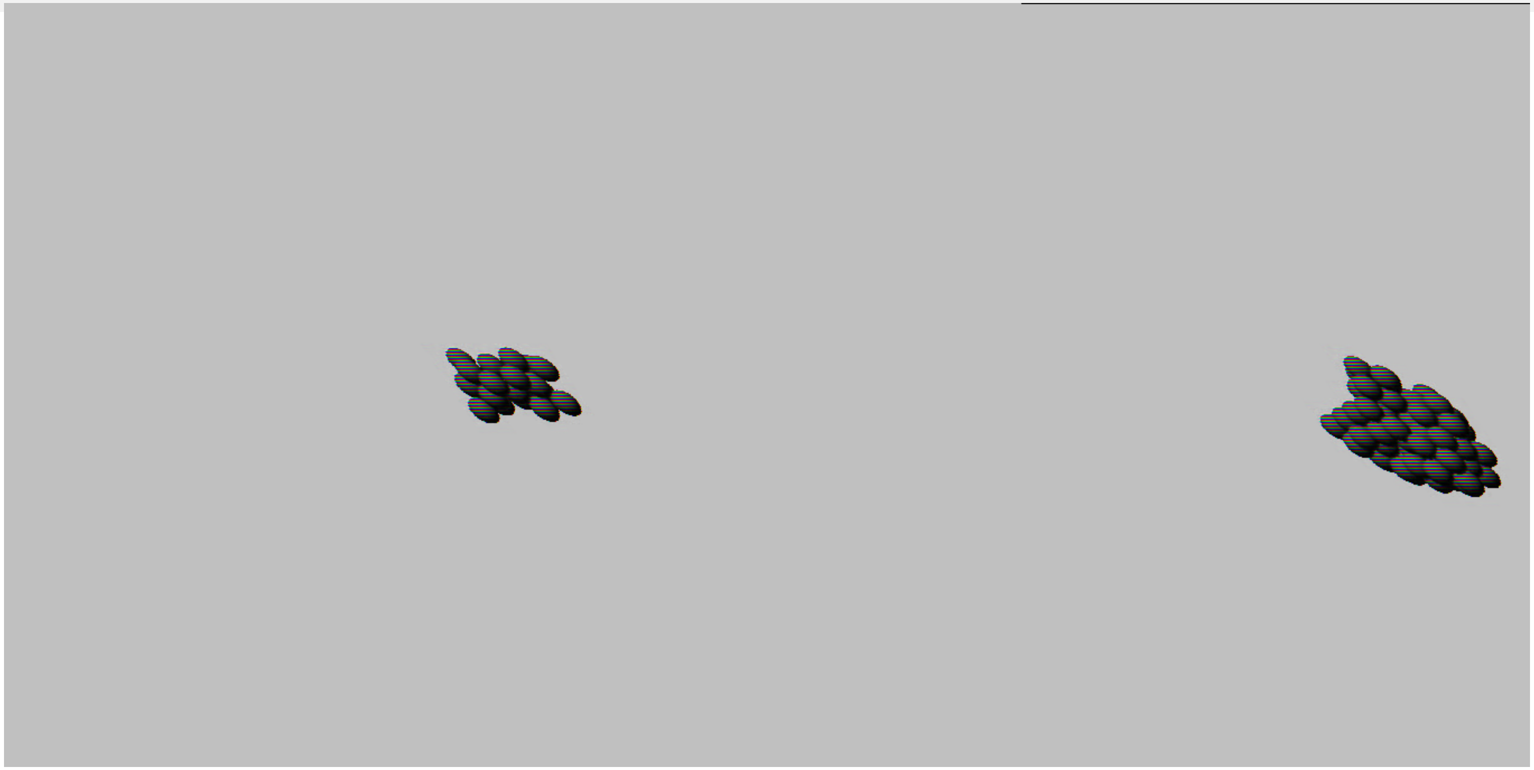
- Each encounter (event) is simulated accurately by the DEM-SD method

- Possible outcomes of a single event:
  - Missed collision
  - Collision
  - Collision and breakup

- On the basis of the actual outcome of the DEM simulation the population is updated

Encounter outcome: missed collision

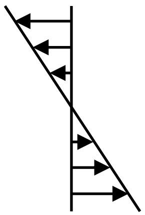


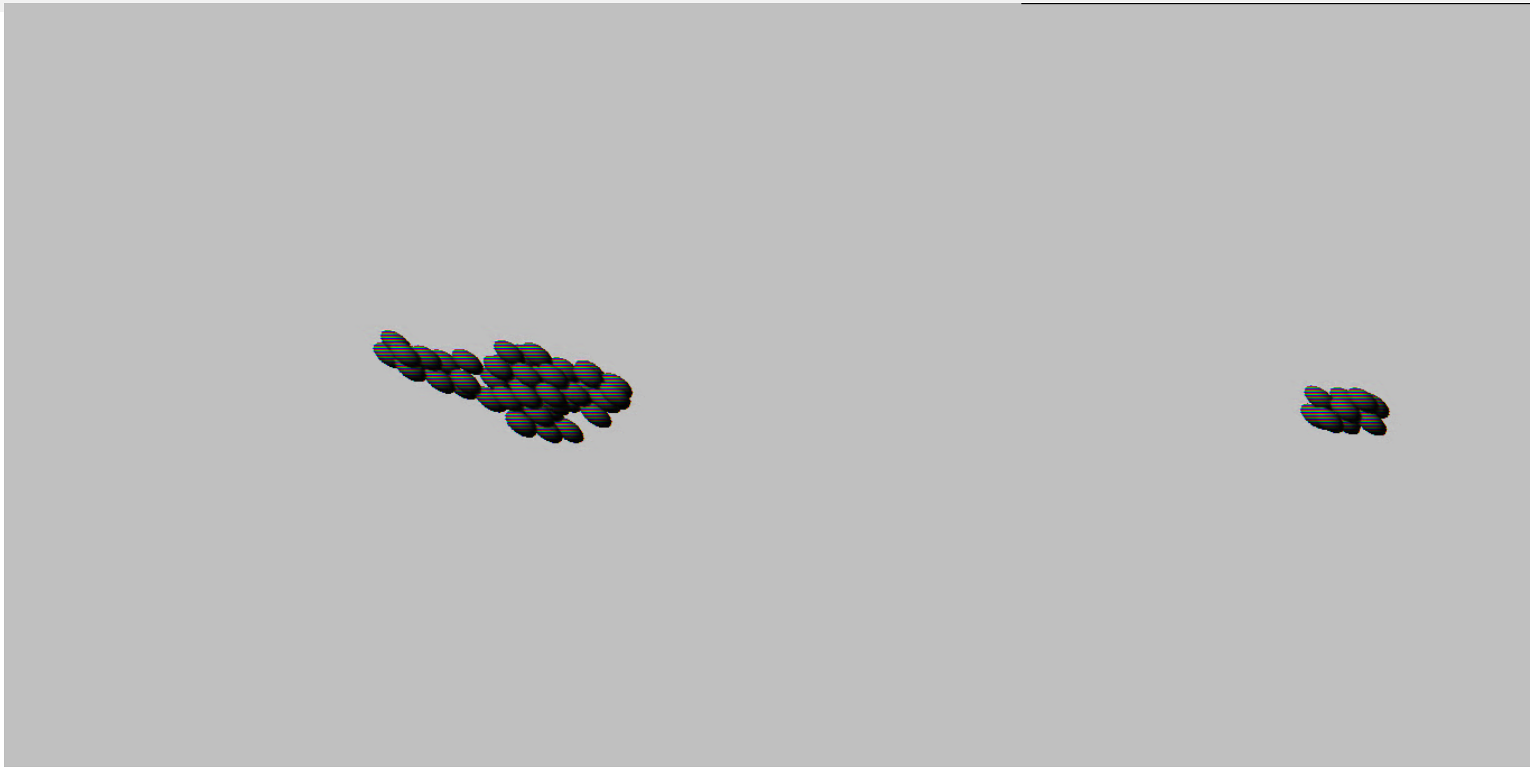


- Possible outcomes of a single event:
  - Missed collision
  - Collision
  - Collision and breakup

missed collision

Encounter outcome: collision



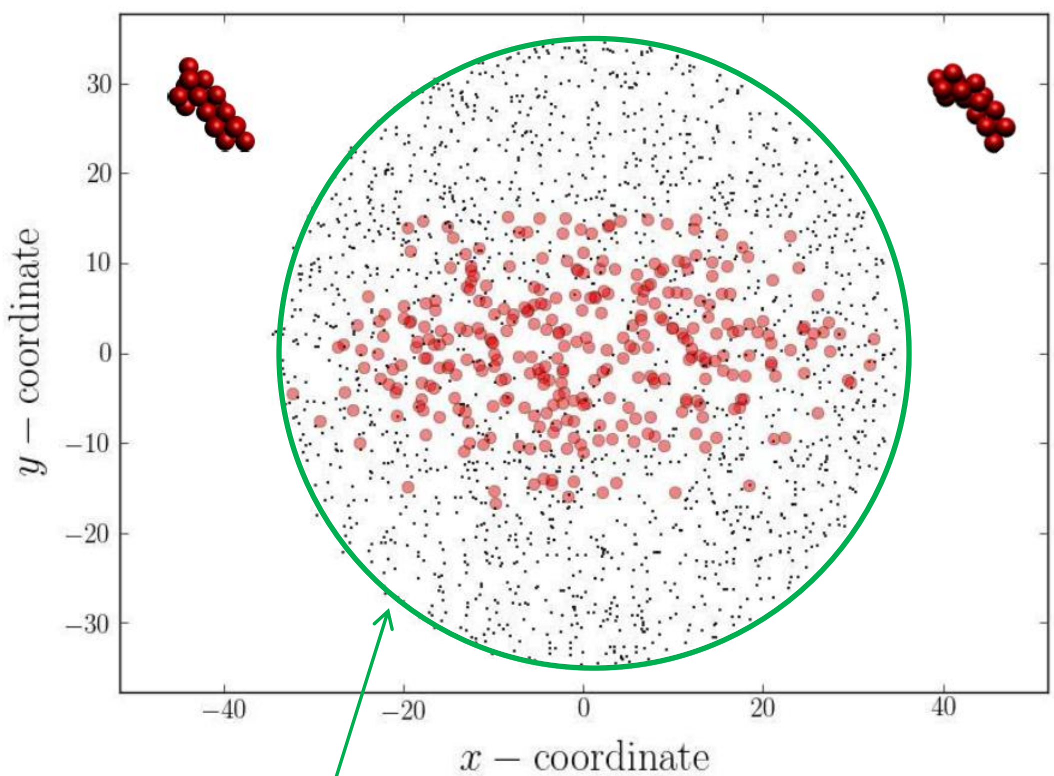


- Possible outcomes of a single event:
  - Missed collision
  - Collision
  - Collision and breakup

collision

Encounter outcome: collision

The probability of actual collision is not very large



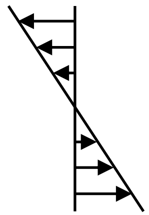
- Possible outcomes of a s

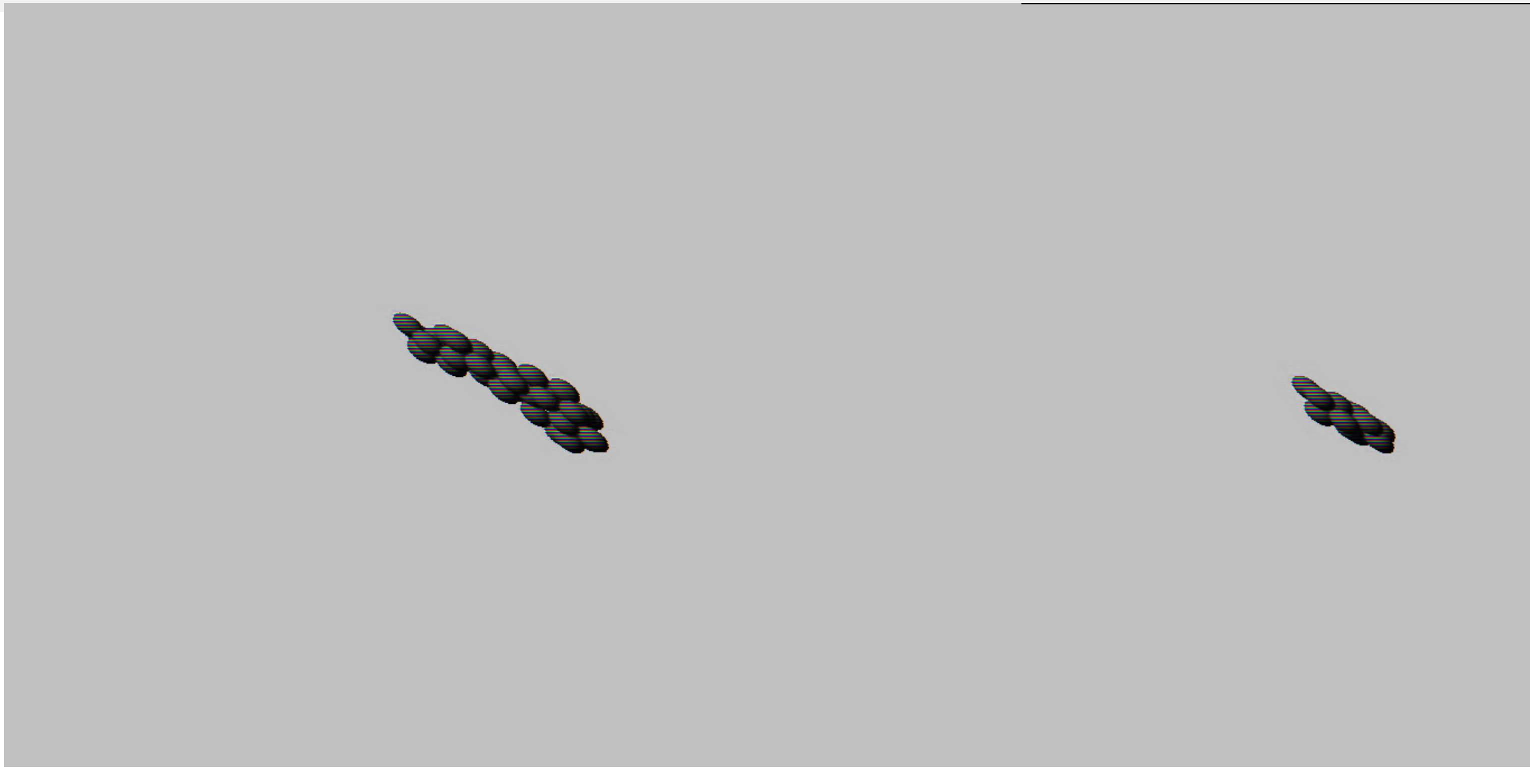
theoretical collision cross-section

collision

- Missed collision
- Collision
- Collision and breakup

Encounter outcome: collision + breakup





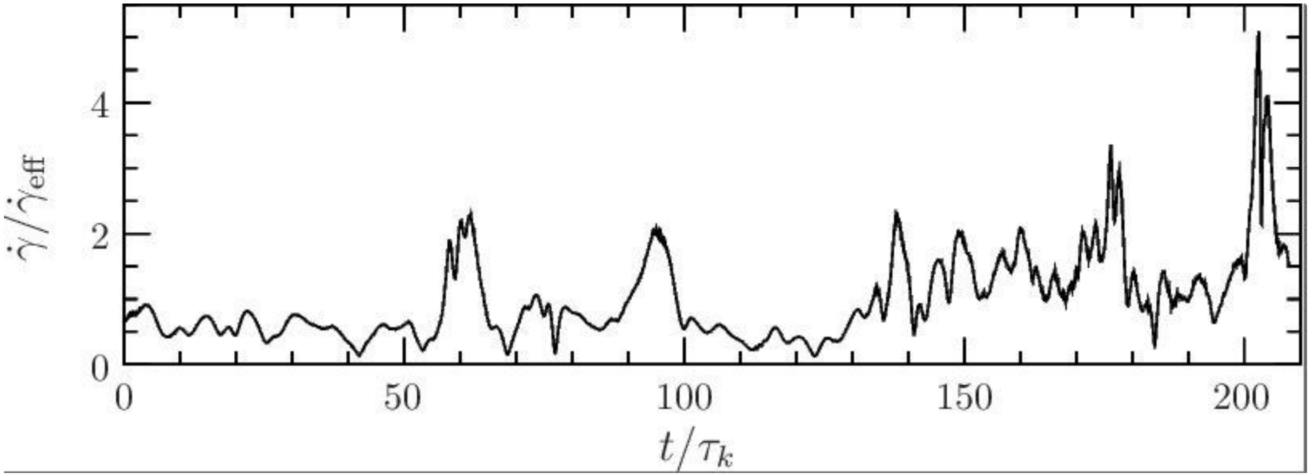
- Possible outcomes of a single event:
    - Missed collision
    - Collision
    - Collision and breakup

collision+breakup

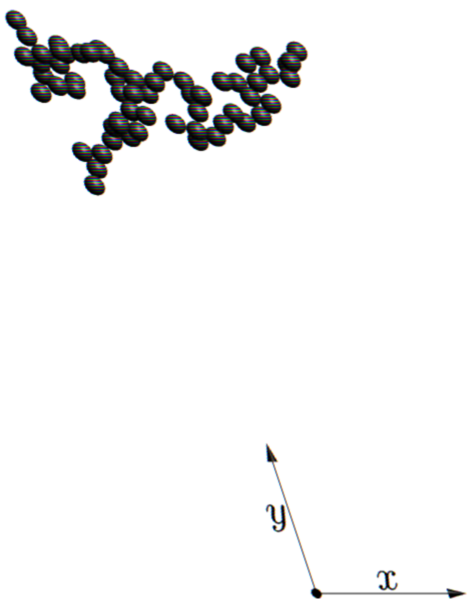
Encounter outcome: collision + breakup

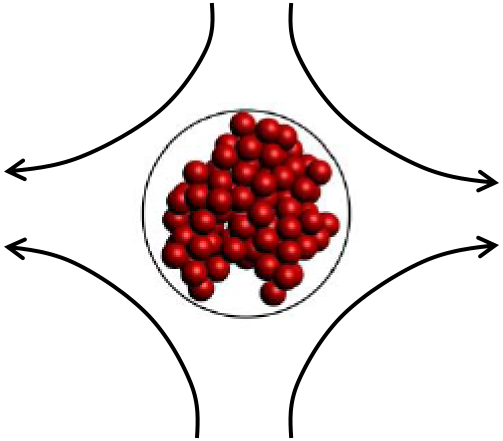
Breakup is not a primary event with its own frequency in a homogeneous stationary shear flow field, as it occurs only when a critical size is exceeded (i.e., shortly after a coalescence event).

This situation is very different from the case of highly non uniform and unsteady shear flow (like in turbulence), where particles can enter region of high strain rate, where they can break up even in the absence of previous coalescence.



Pure breakup in an unsteady flow field

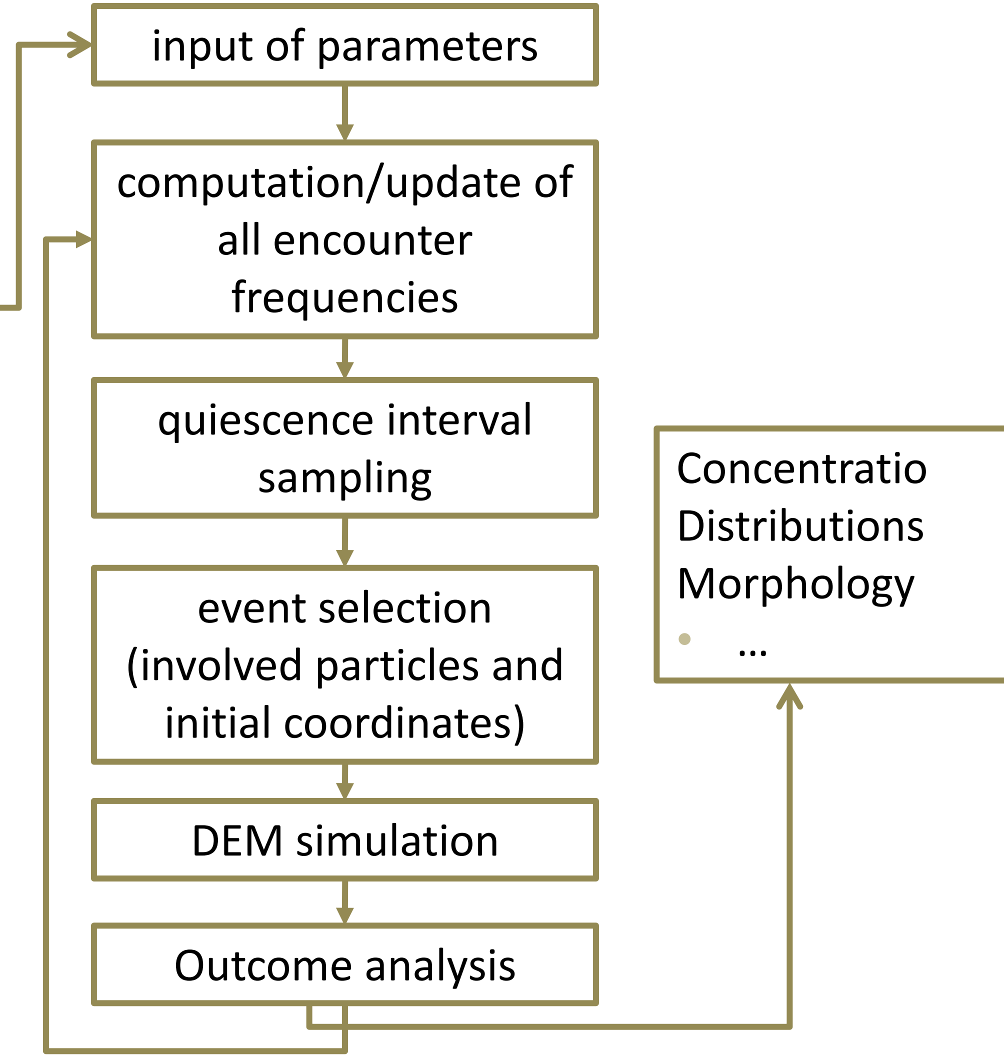




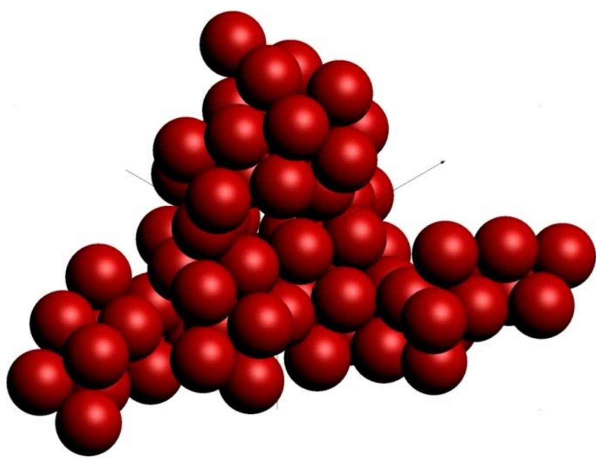
plane elongational flow with continuously increasing strain rate

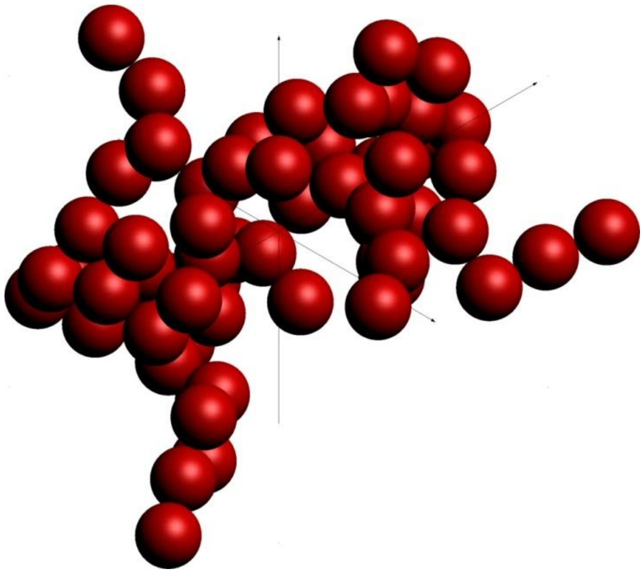
Setup and simulation scheme

number of particles	200 [150 – 300]
solid fraction	10^{-4}
shear rate	$(1\text{-}5)\cdot10^{4}$ s^{-1}
temperature	298 K
viscosity	10 – 150 cP
Hamaker constant	$0.95 \cdot 10^{-20}$ J
monomer radius	500 nm
elastic modulus	3.4 GPa



Results

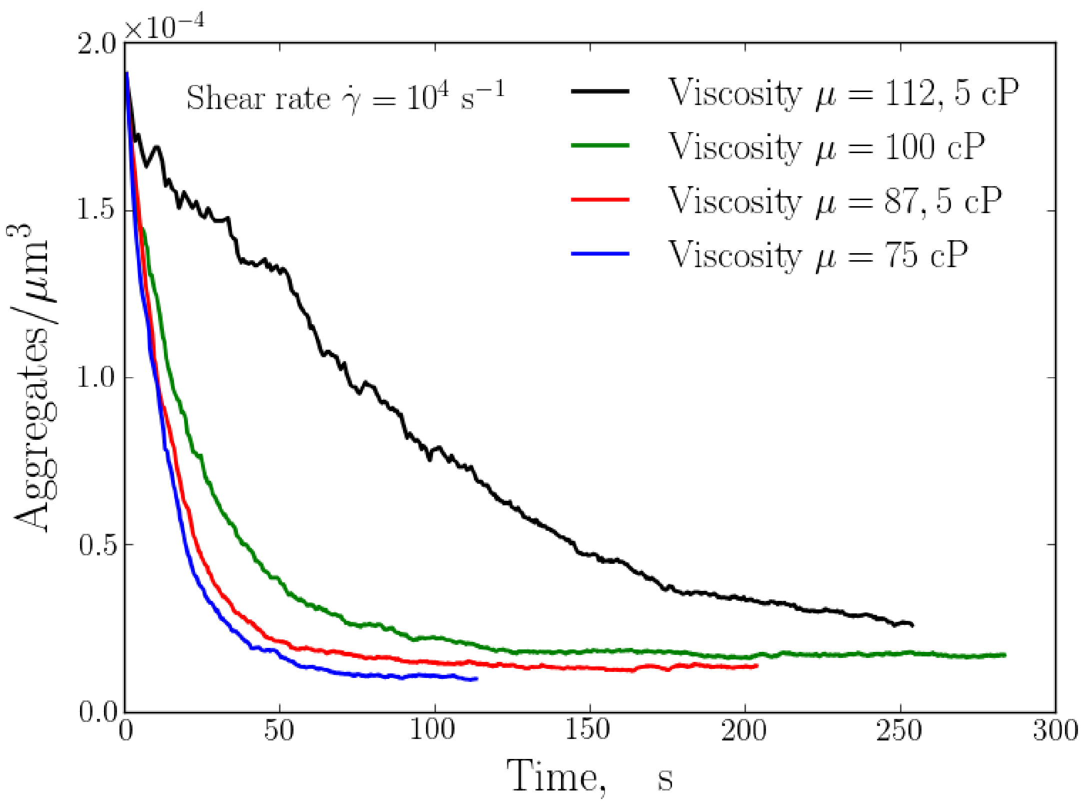




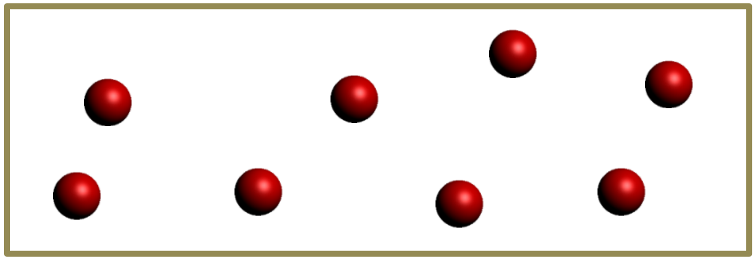
<u>Case a</u>) only normal (i.e., attractive) interaction at interparticle contacts - no resistance to mutual rotation or sliding –
compact soft aggregates

<u>Case b</u>) fully rigid interparticle contacts –
highly porous stiff aggregates

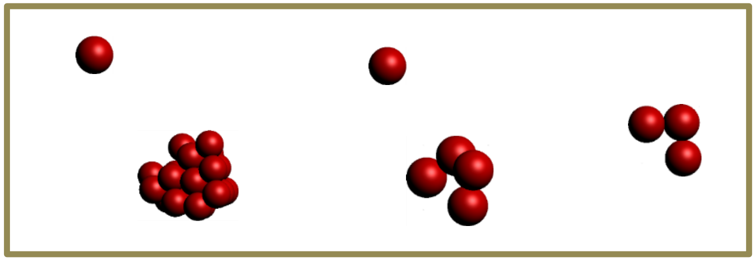
Aggregate number density (soft aggregates)



Initial state

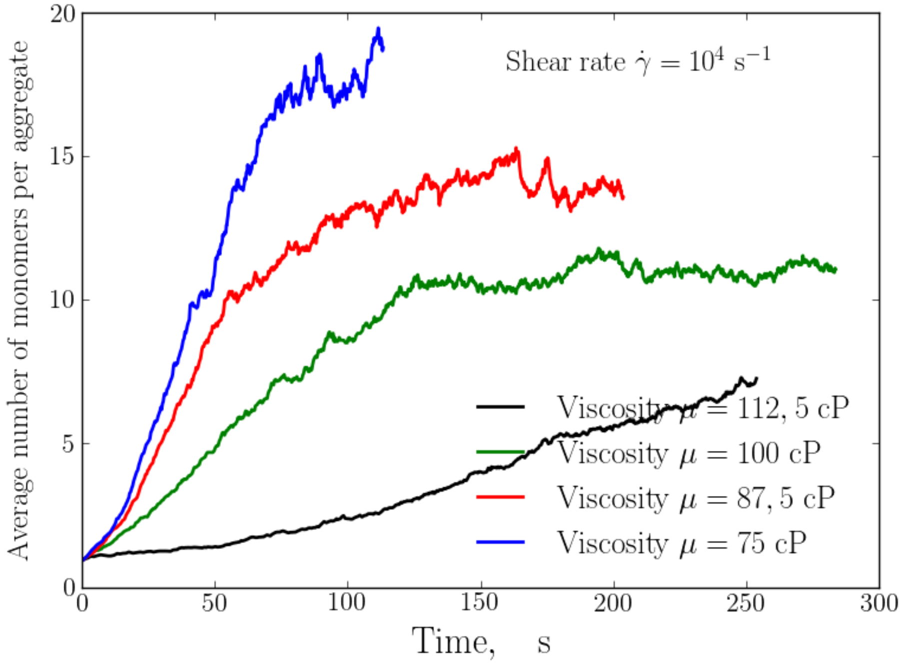


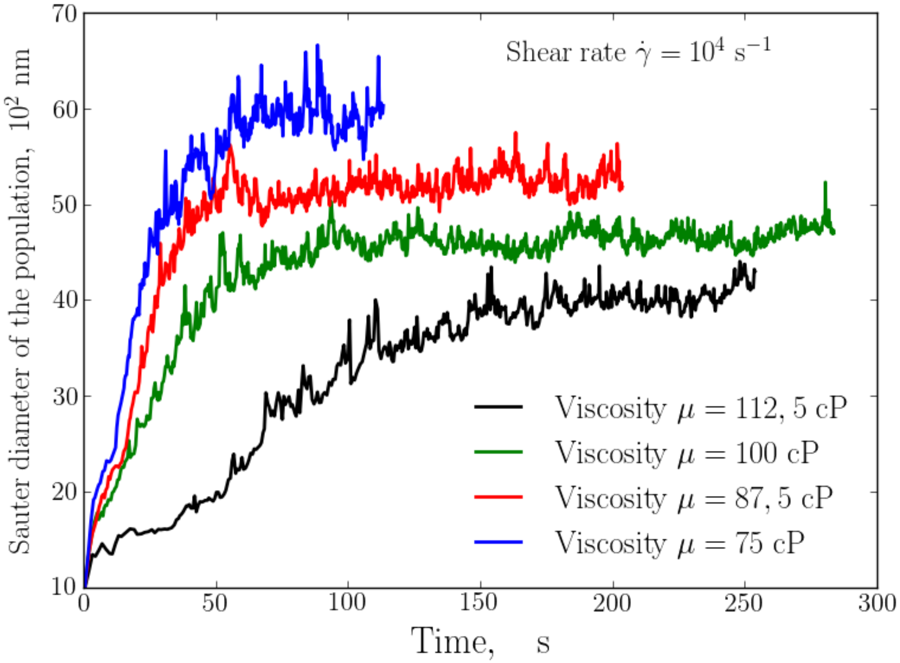
Final state



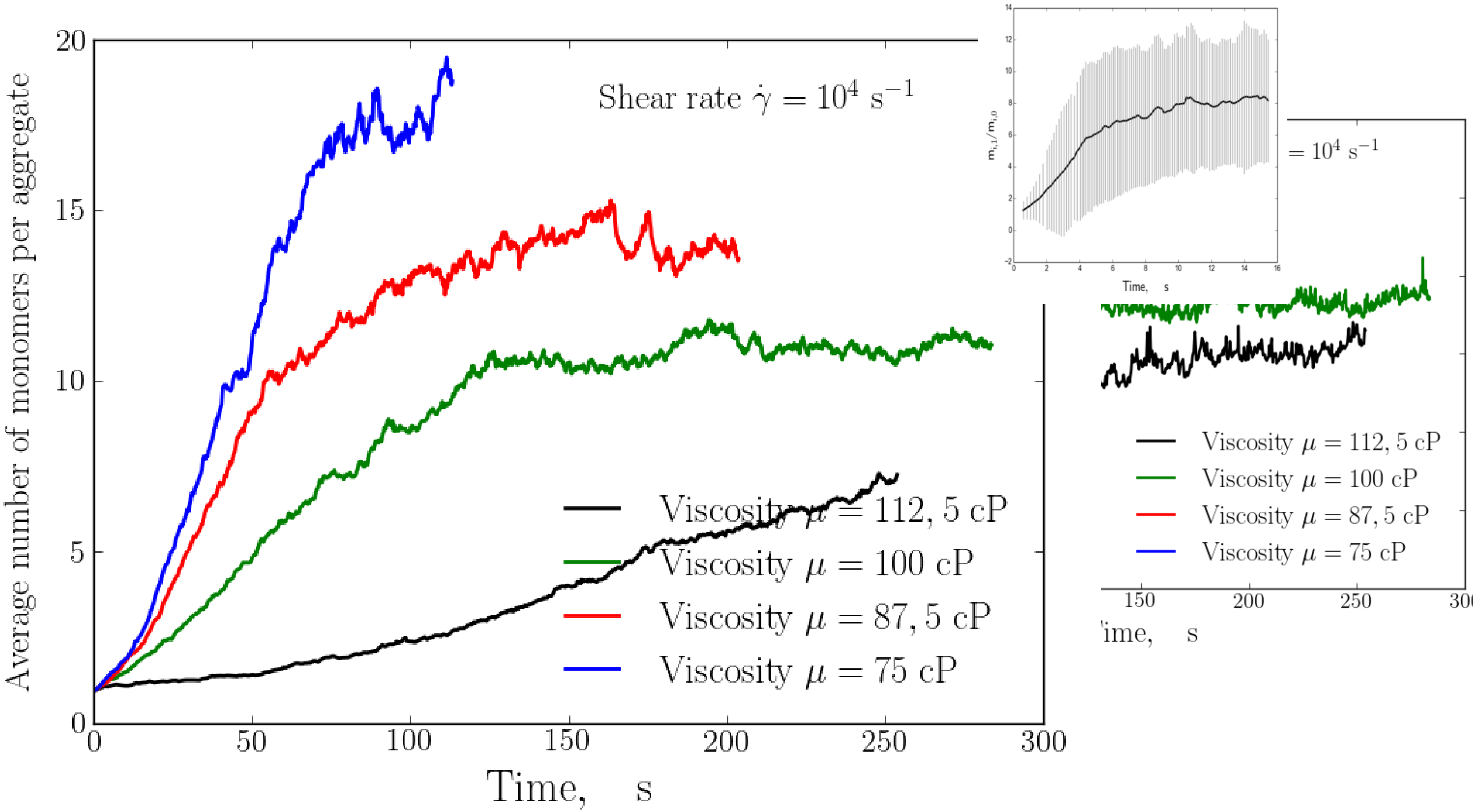
Actual number of aggregates ≈ 200

Mean aggregate size

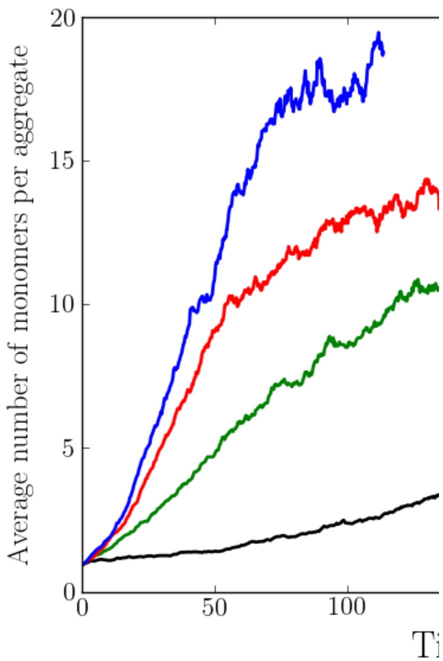


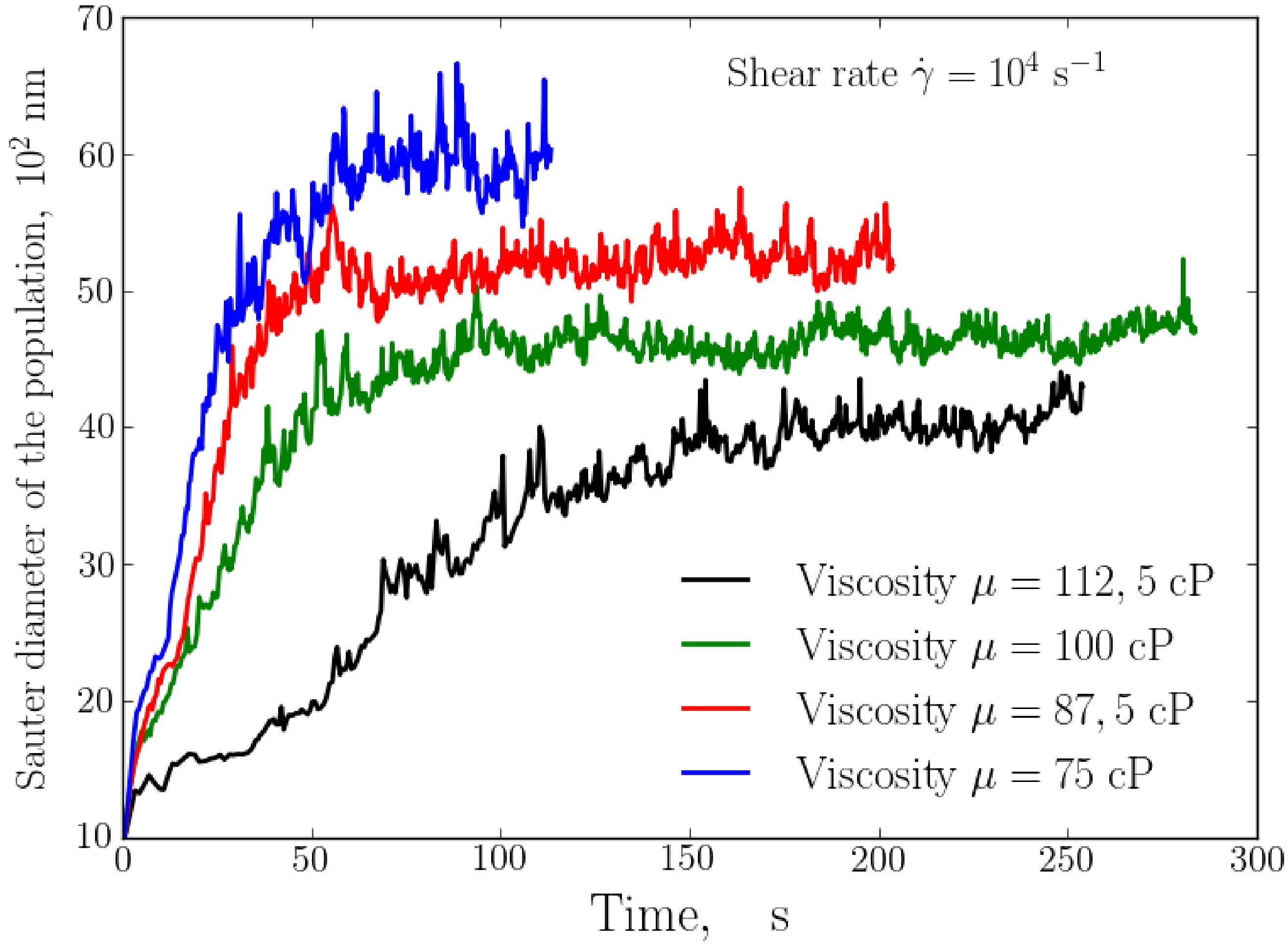


Mean aggregate size



Mean aggregate size

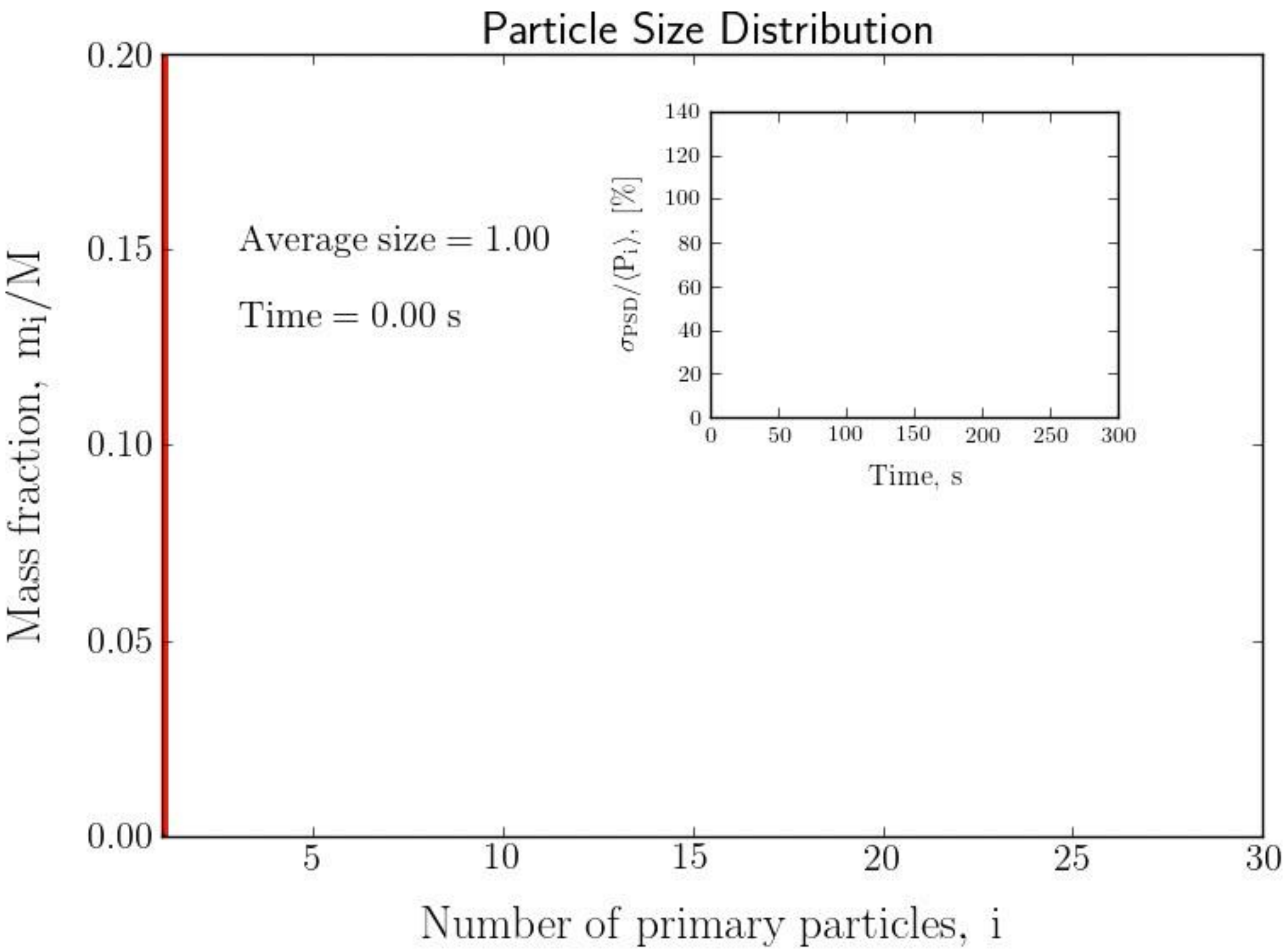




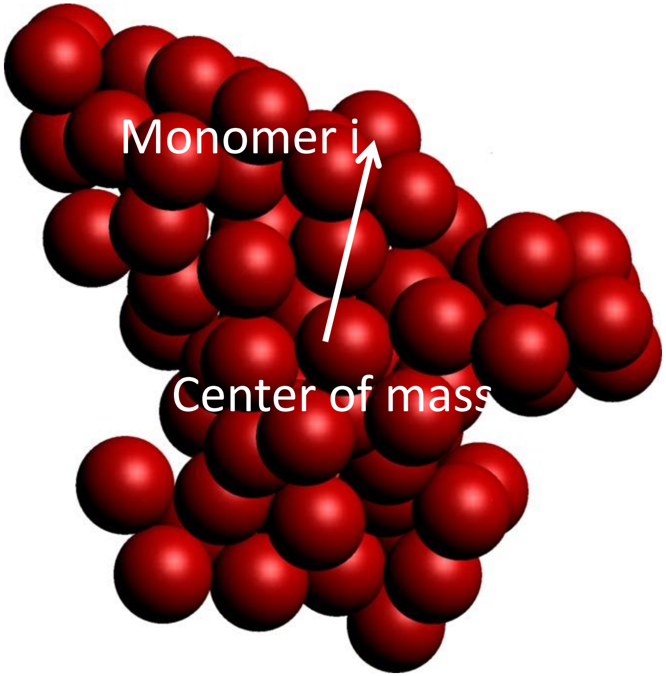
Time Evolution of the Particle Size Distribution

viscosity = 100 cP

shear rate = 10^4 s^{-1}



Aggregate characterization – Fractal dimension (soft aggregates)



$$R_g^2 = \frac{1}{P}\sum_{i=1}^{P}\left|\mathbf{r}_i - \mathbf{r}_{cm}\right|^2$$

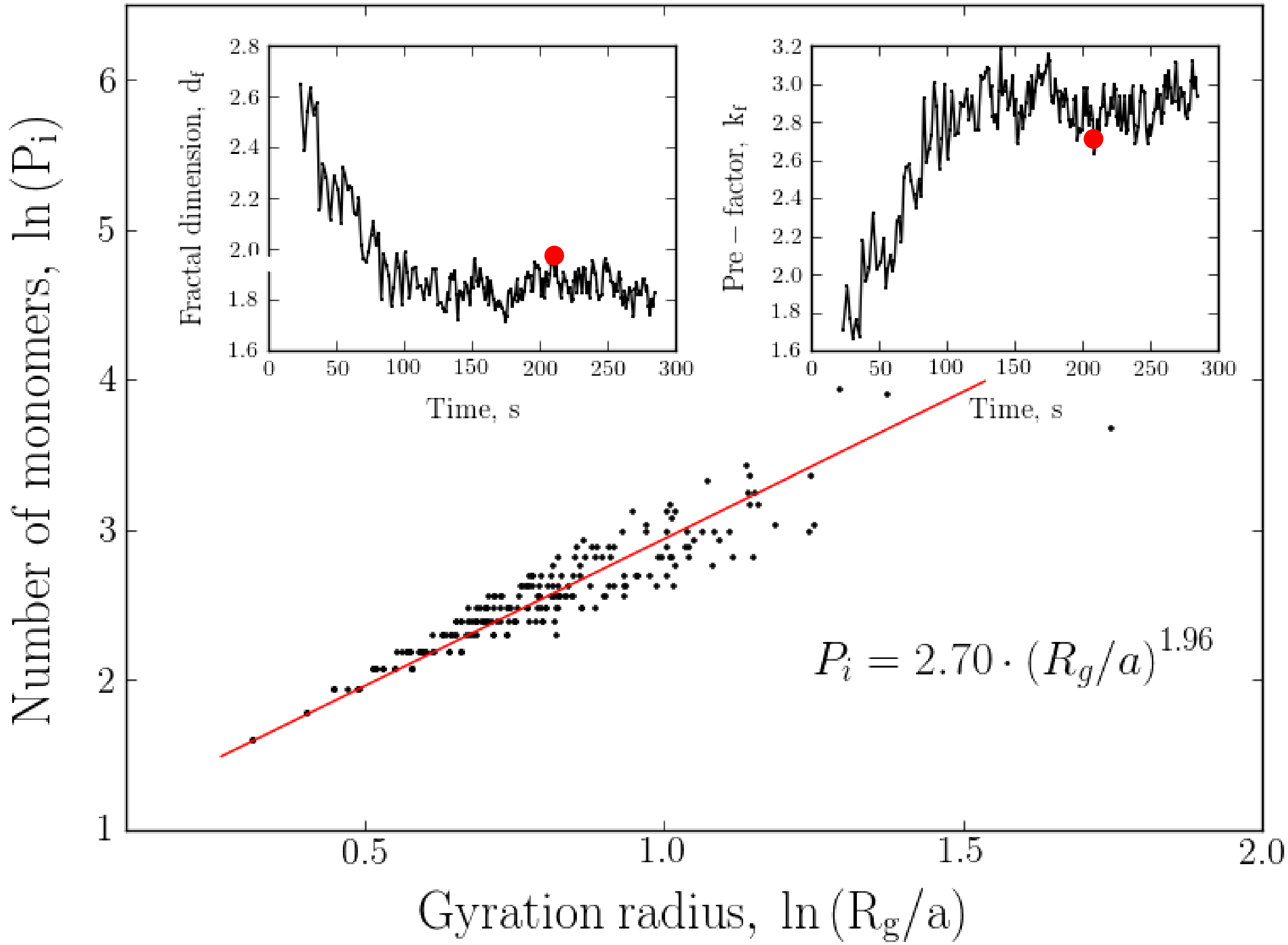
$$P = k_f\left(R_g/a\right)^{d_f}$$

The fractal dimension is expected to be around 3 for compact aggregates

Aggregate characterization – Fractal dimension

$$P = k_f \, (R_g/a)^{d_f}$$

The low value of the exponent is a consequence of the non-rigid structure of the aggregates. Bigger aggregates are more elongated



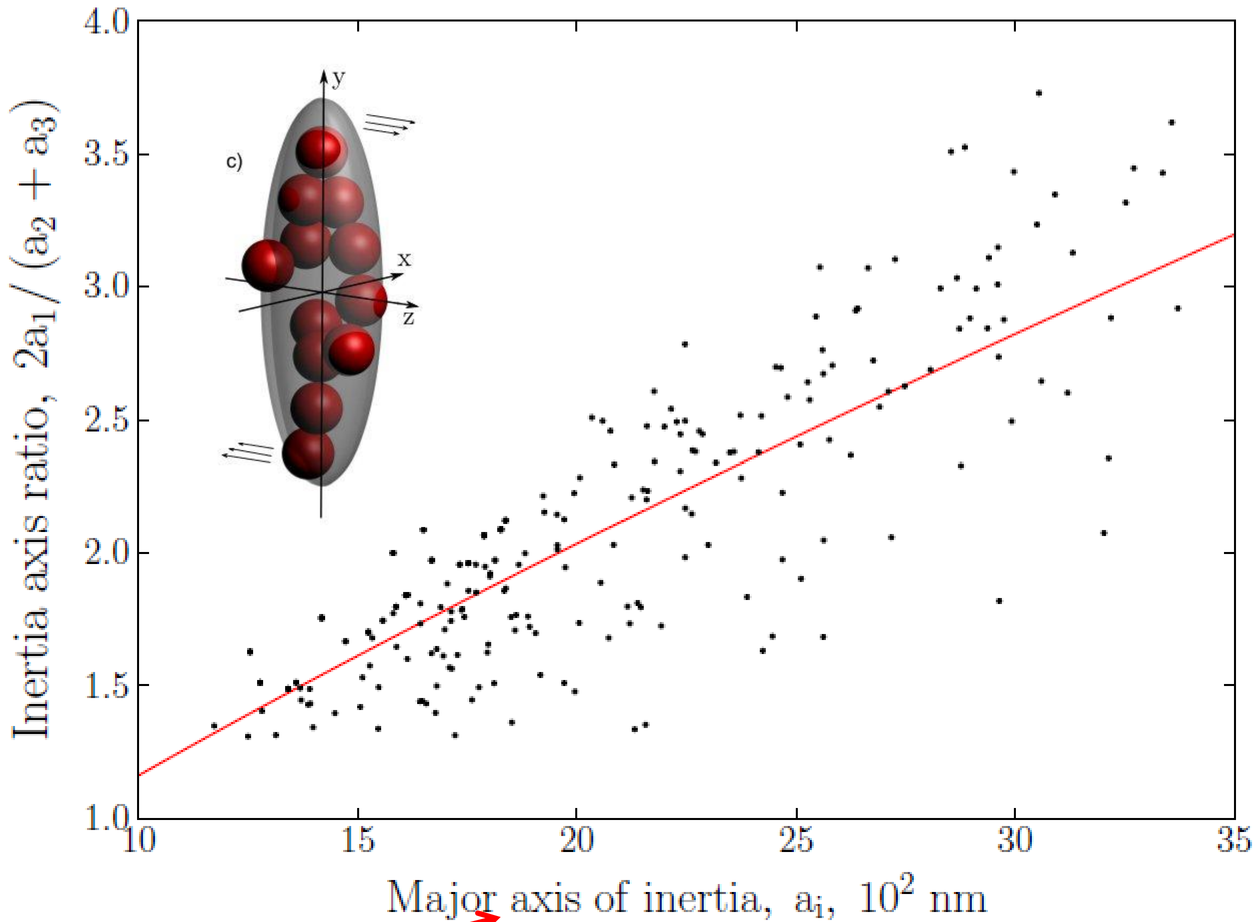
viscosity = 100 cP shear rate = 10^4 s^{-1}

Aggregate characterization – Fractal dimension

$$P = k_f \left(R_g/a\right)^{d_f}$$

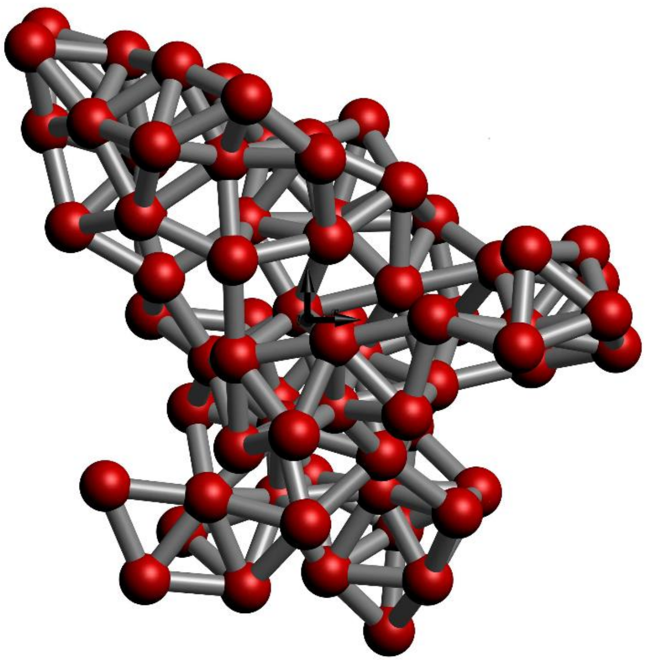
The low value of the exponent is a consequence of the non-rigid structure of the aggregates. Bigger aggregates are more elongated

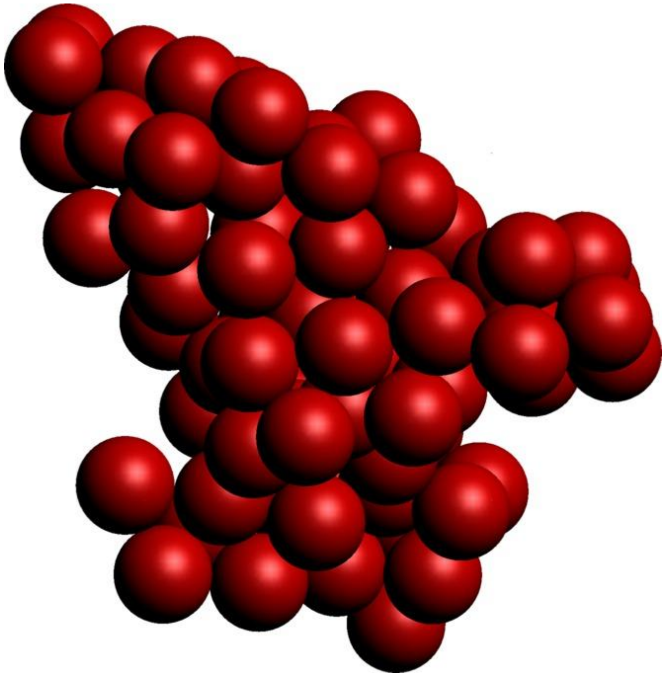
Index of shape anisotropy



Aggregate size

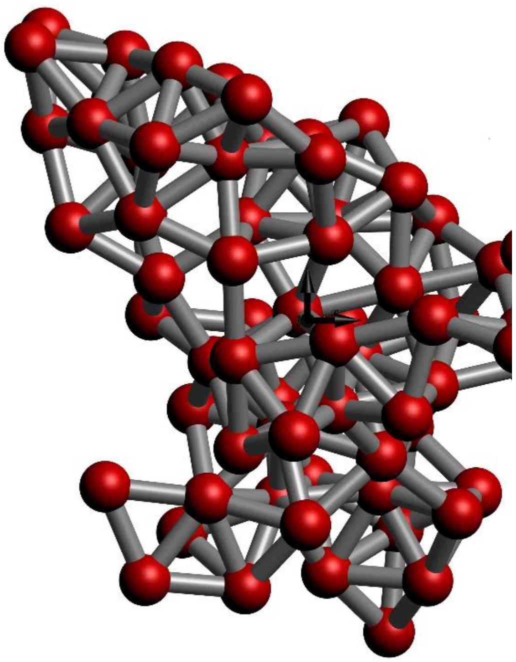
Aggregate characterization – Coordination (soft aggregates)

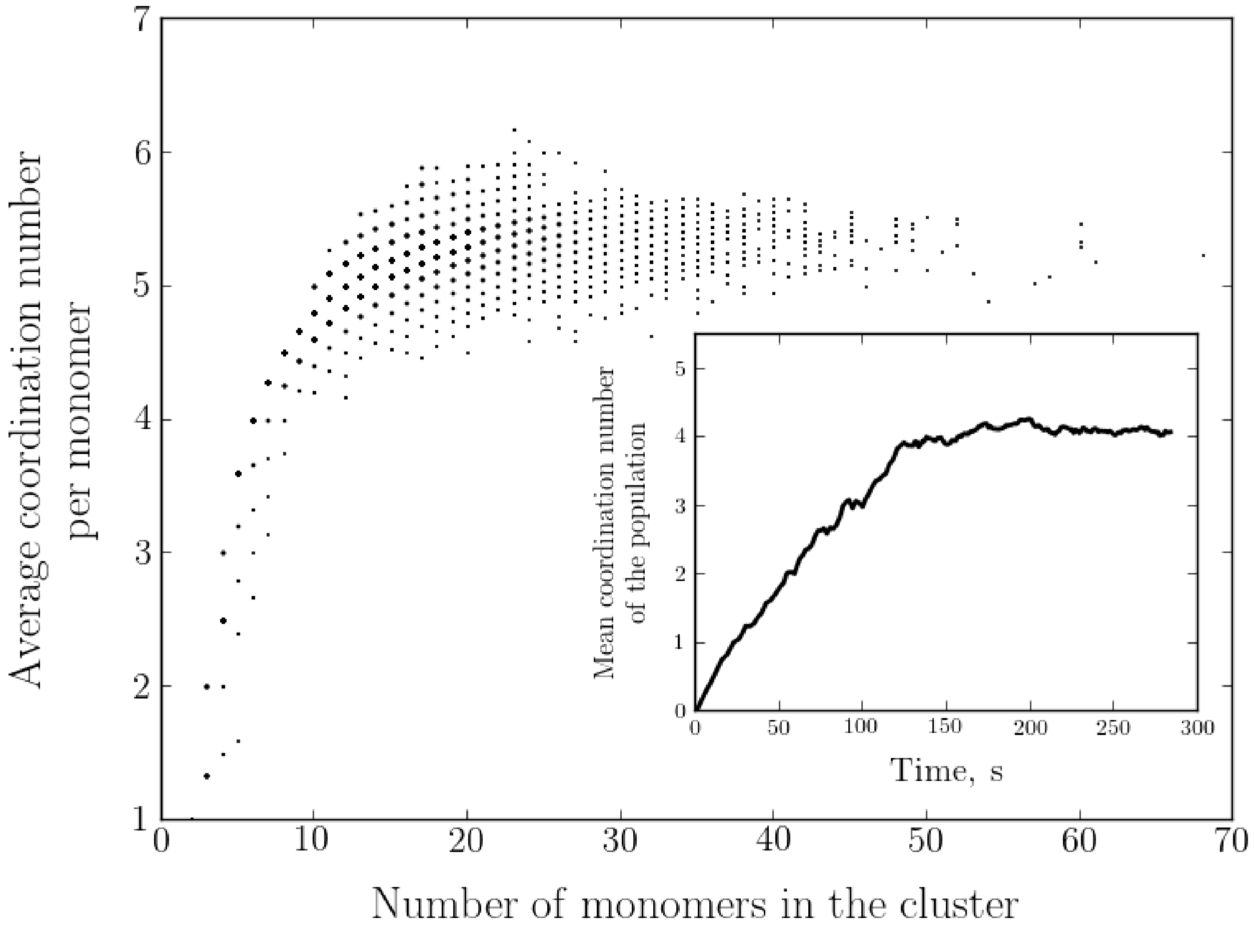




Aggregate characterization – Coordination

viscosity = 100 cP   shear rate = 10^4 s^{-1}

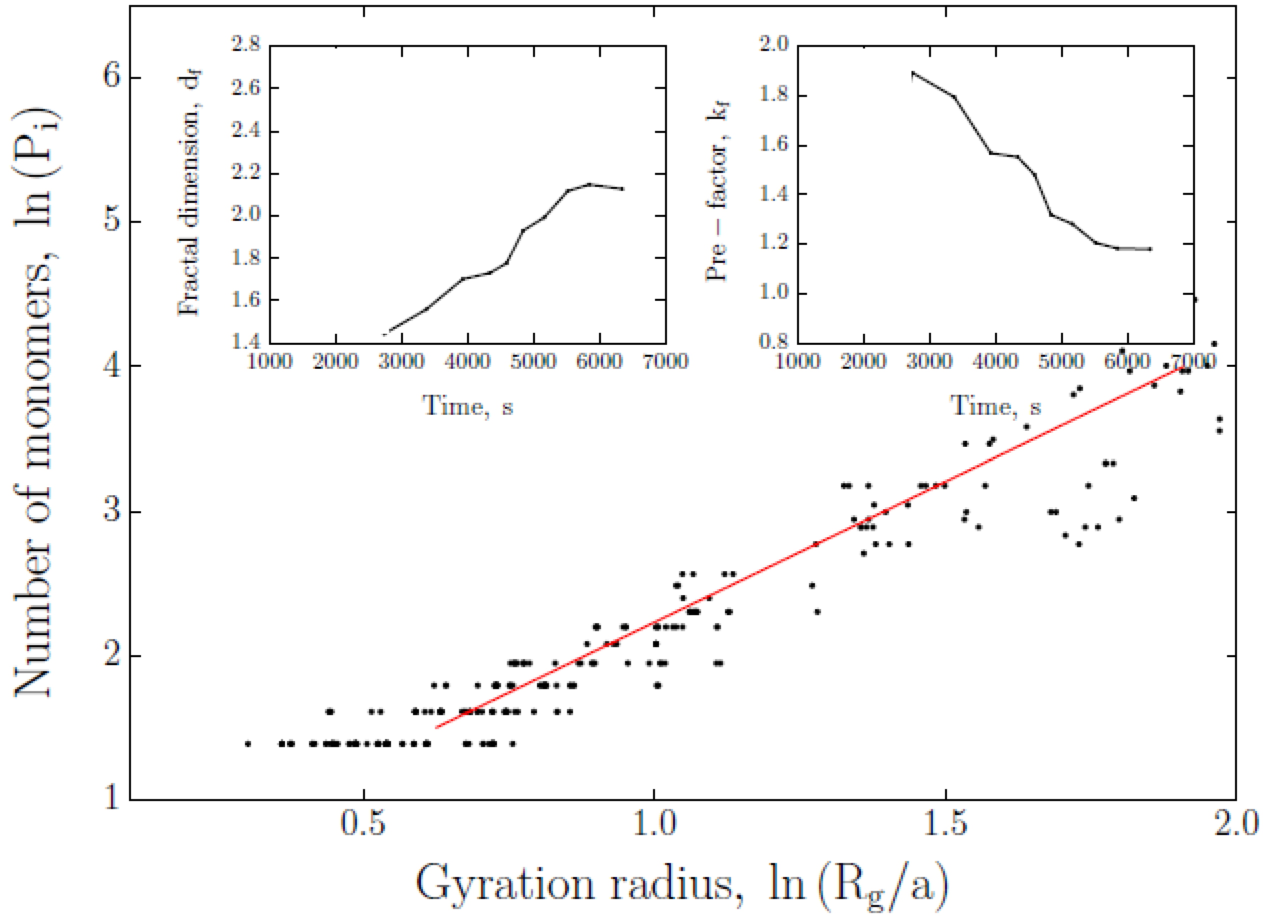




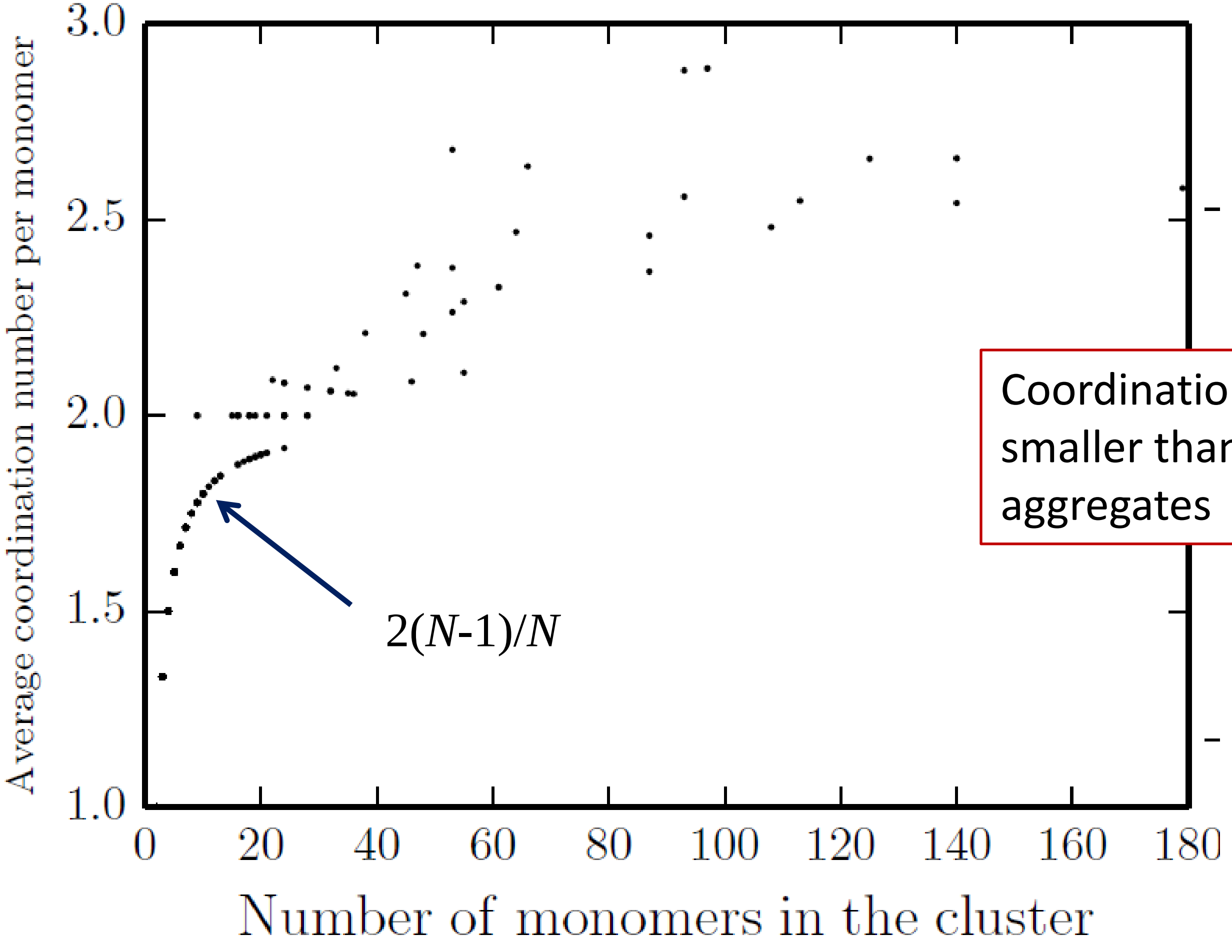
Aggregate characterization – Fractal dimension (stiff aggregates)

$$P = k_f \left(R_g/a\right)^{d_f}$$

Fractal dimension increases from 1.4 to 2.1

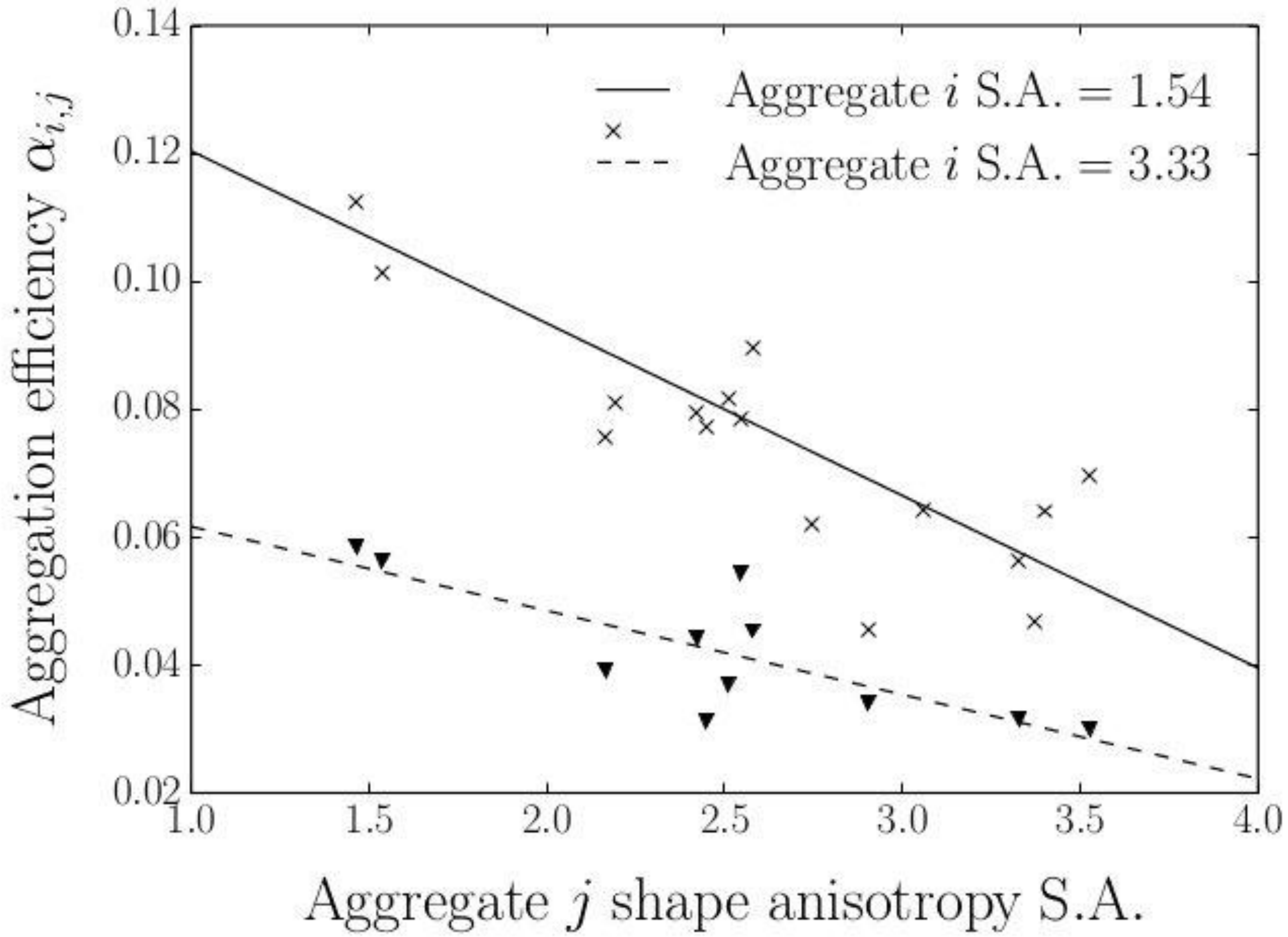


Aggregate characterization – Coordination (fully rigid contacts)



Coordination is much smaller than in soft aggregates

Aggregation efficiency and shape anisoptropy



Shape anisotropy has the major effect on aggregation efficiency

Conclusions

The developed method has been proven to be promising to reproduce the dynamical behavior of the suspension

- The **DEM** model, built in the framework of **Stokesian Dynamics**, is able to describe, at best of our knowledge, hydrodynamic and colloidal interaction between particles, returning **physically reliable** results in reasonable time

- The combination of a **Monte Carlo** approach and a DEM model allows to circumvent the high computational cost needed to dynamically simulate **in full detail** a representative sample of the population

Expected outcomes:

- Evaluation of aggregation and breakup rates to be used effectively for large scale simulations (CFD, population balance)

Thank you for your attention