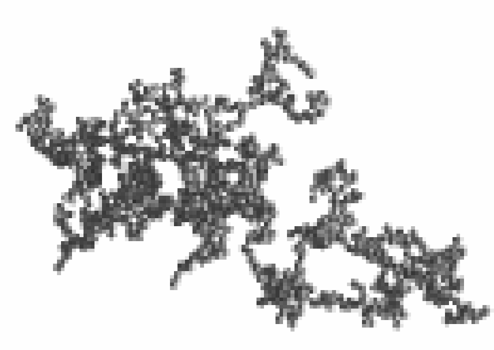

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Aggregation and Breakage of Nanoparticle Dispersions in Heterogeneous Turbulent Flows

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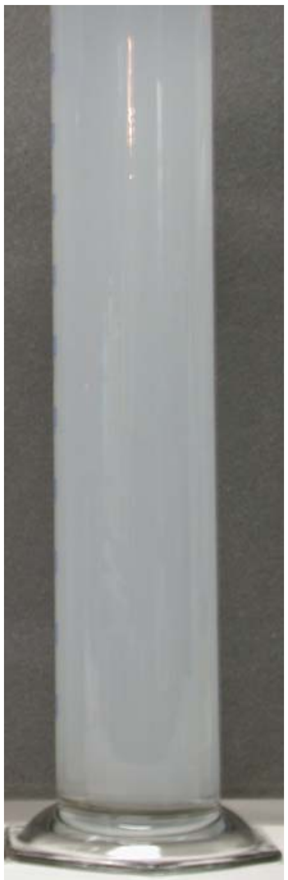
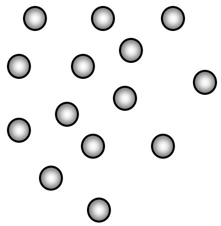
CFD in Chemical Reaction Engineering
Barga, Italy, June 2005

Problem definition - coagulation process

Dispersion of stable primary particles



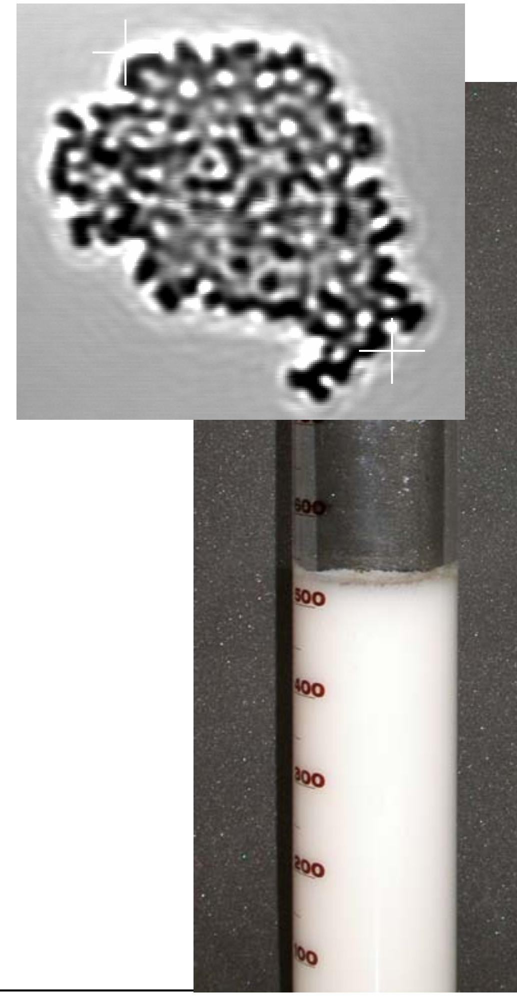


destabilization

Coagulator types:

Stirred tank
Couette device
Pipe

Aggregates / Granules



10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3}

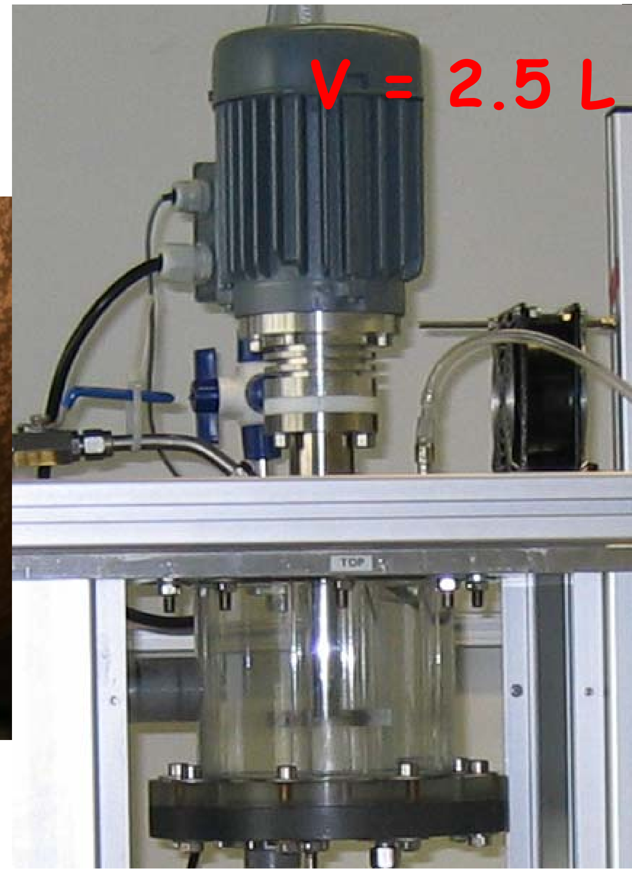
[m]

Problem definition - coagulation process

To have good product quality:

- appropriate morphology
- effective mixing

→ **Turbulent flow**



Stirred tank

Taylor-Couette device

Particle/aggregate characterization technique

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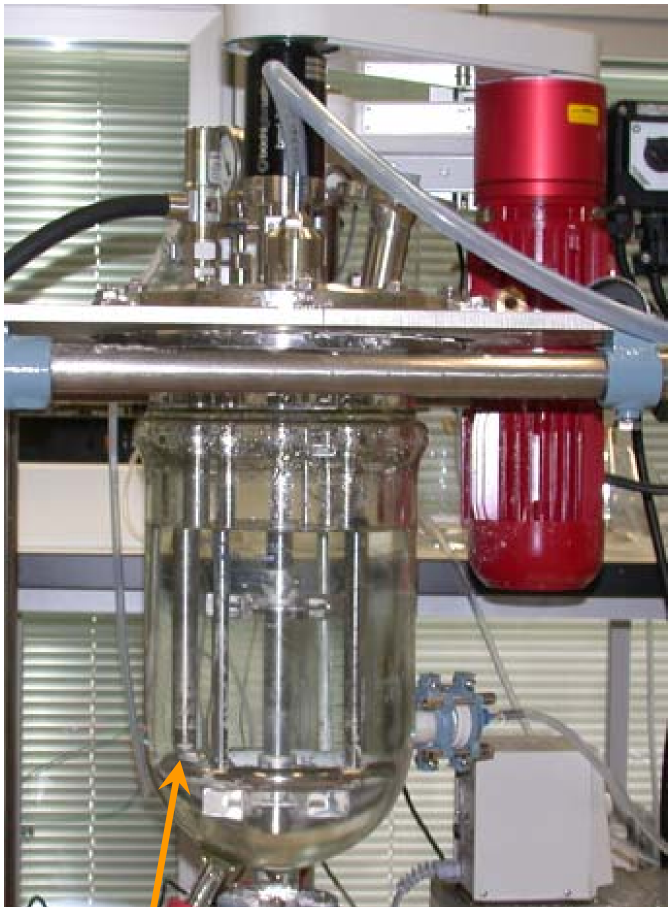
Focused Beam Reflectance Method (LASENTEC)



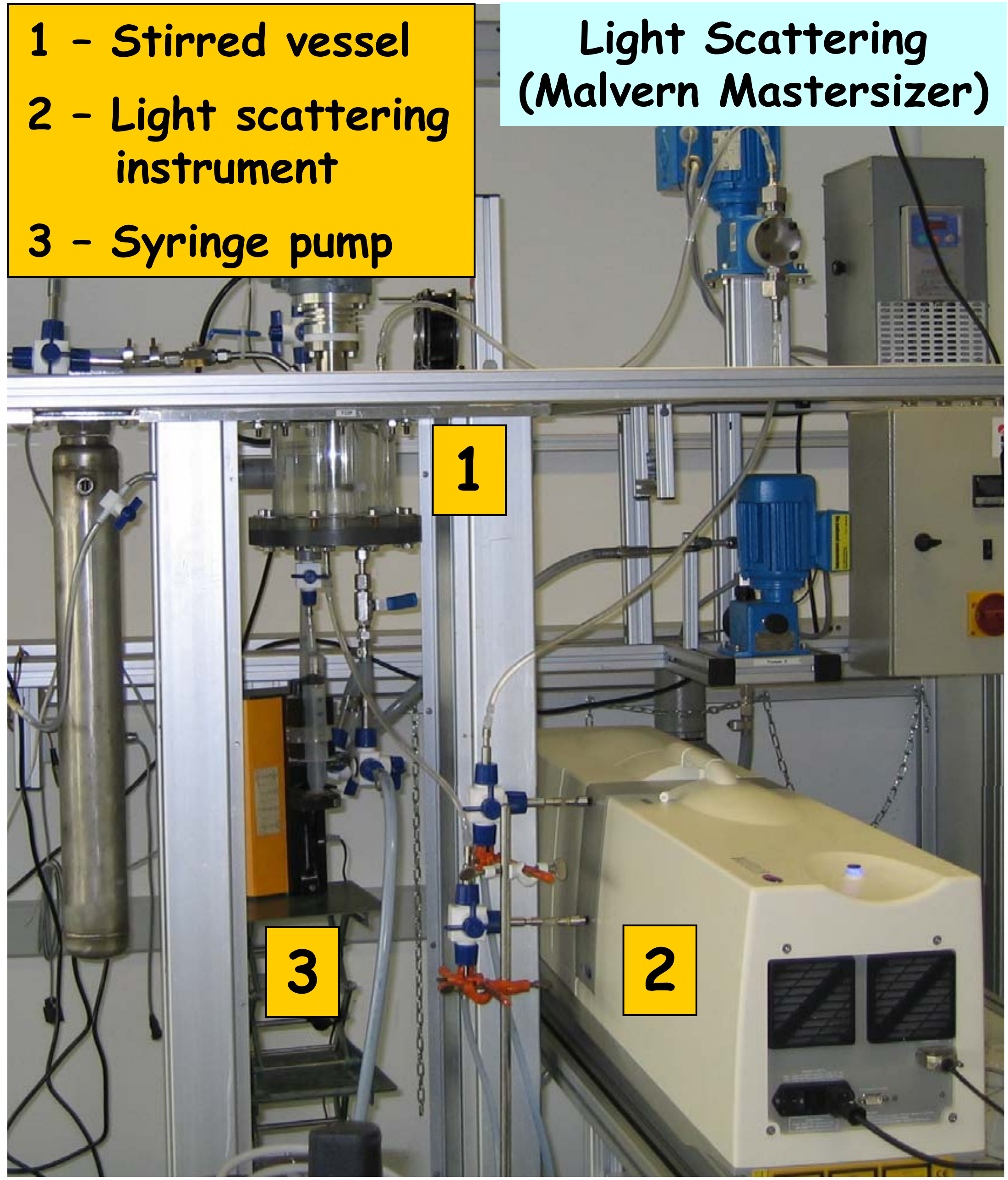
Probe of FBRM

1 – Stirred vessel

2 – Light scattering instrument

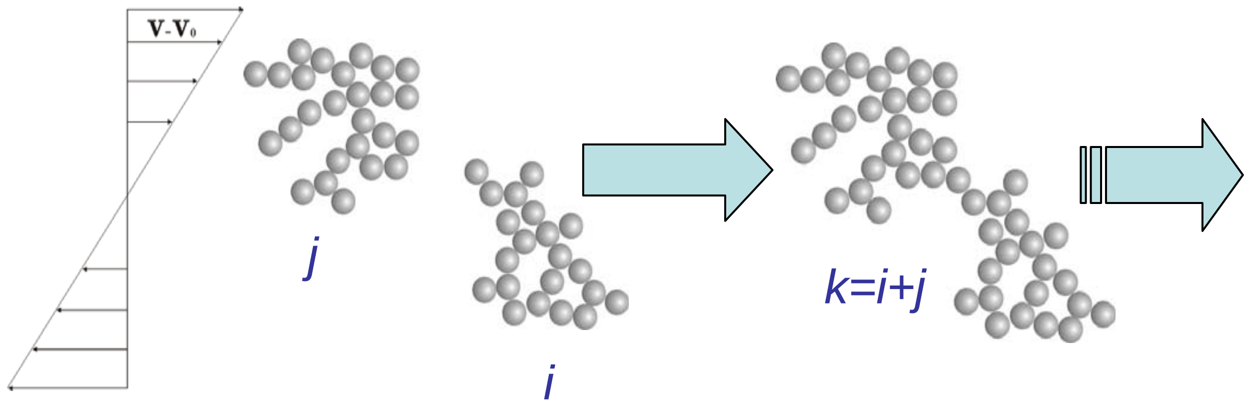
3 – Syringe pump

Light Scattering (Malvern Mastersizer)



Aggregation and Breakage kinetics

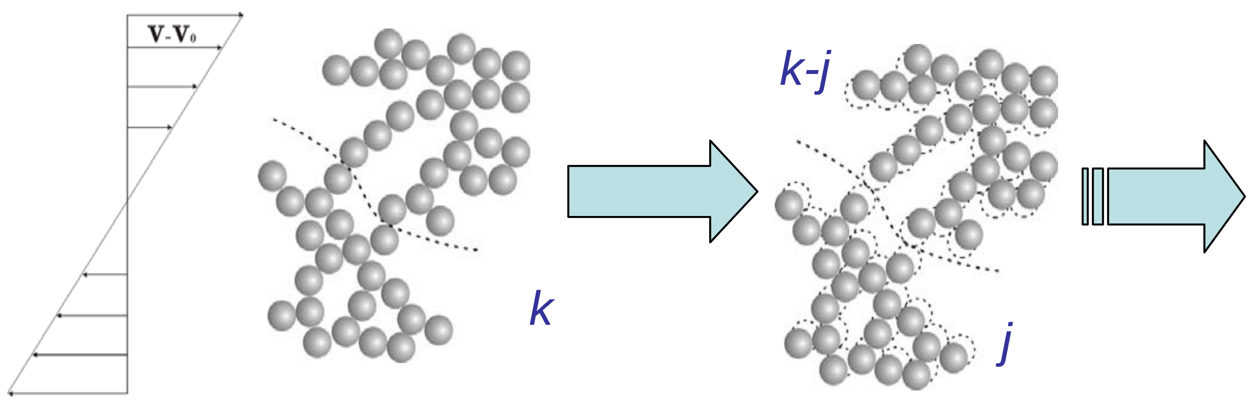
Aggregation



$$K_{i,j}^{A} N_i N_j$$

Aggregation Rate

Breakage



$$K_k^B N_k$$

Breakage Rate

Assumption about daughter distribution function

Population Balance Equation

Reynolds-averaged mass balance ("CFD & PBE"): (PBE mass based)

$$\frac{\partial n(\xi;\mathbf{x},t)}{\partial t} + \frac{\partial}{\partial x_i}\left[\langle u_i\rangle_t\, n(\xi;\mathbf{x},t)\right] - \frac{\partial}{\partial x_i}\left[D_t \frac{\partial n(\xi;\mathbf{x},t)}{\partial x_i}\right] =$$

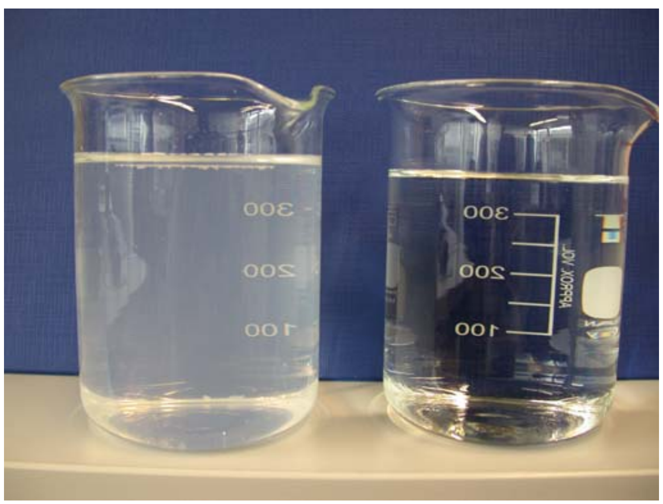
Aggregation source term

$$\frac{1}{2}\int_1^{\xi} K^A_{\xi-\xi',\xi'}\, n(\xi-\xi';\mathbf{x},t)\; n(\xi';\mathbf{x},t)\,\mathrm{d}\xi' - n(\xi;\mathbf{x},t)\int_1^{\infty} K^A_{\xi,\xi'}\, n(\xi';\mathbf{x},t)\,\mathrm{d}\xi'$$

$$+\int_{\xi}^{\infty} K^B_{\xi'}\, b(\xi|\xi')\; n(\xi';\mathbf{x},t)\,\mathrm{d}\xi' - K^B_{\xi}\, n(\xi;\mathbf{x},t)$$

Breakage source term

Only unknown are the values of aggregation and breakage kernels



There are several numerical approaches to solve this equation:

- **Classes method**
- **Method of moments***
- **Monte Carlo method**

...

$b(\xi\,|\,\xi')$ - Daughter distribution function of produced fragments

Aggregation and Breakage rate expressions (kernels)

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Aggregation kernel:

$$K^{A}_{\xi,\xi'} = K^{BA}_{\xi,\xi'} + K^{SA}_{\xi,\xi'}$$

$$K^{BA}_{\xi,\xi'} = \frac{2k_B T}{3\mu}\frac{1}{W}\left(\xi^{-1/d_f} + \xi'^{-1/d_f}\right)\left(\xi^{1/d_f} + \xi'^{1/d_f}\right)$$

$$K^{SA}_{\xi,\xi'} = \alpha_A G R_p^3 \left(\xi^{1/d_f} + \xi'^{1/d_f}\right)^3$$

Breakage kernel:

$$K^{B}_{\xi} = P_1(G)\left(\xi^{1/d_f}\right)^{P_3}$$

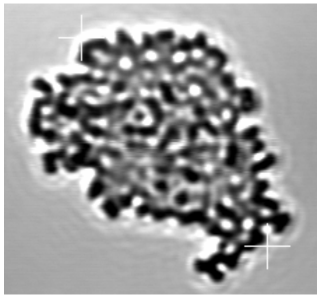
α_A, P_1, P_3, d_f – from experiment or assume

G – either from experiment (**difficult**) or from CFD

$$G = \left(\frac{\varepsilon}{\nu}\right)^{1/2}$$

Fractal scaling:

$$\frac{R_\xi}{R_p} \propto \xi^{1/d_f}$$



Occupied volume fraction:

$$\phi_{OCC} = \int_1^\infty n(\xi)\; V_\xi$$

$$\phi_{occ} \cong 0.5$$

gelation occurs

Connection to light scattering

$$\frac{\langle R_g \rangle}{R_p} = \sqrt{\frac{\sum_{i=1}^{N} w_i \xi_i^{2(1+1/d_f)}}{\sum_{i=1}^{N} w_i \xi_i^2}}$$

w_i – weights of quadrature app.
ξ_i – abscissas of quadrature app.

Solution of PBE - QMOM vs. fixed pivot method

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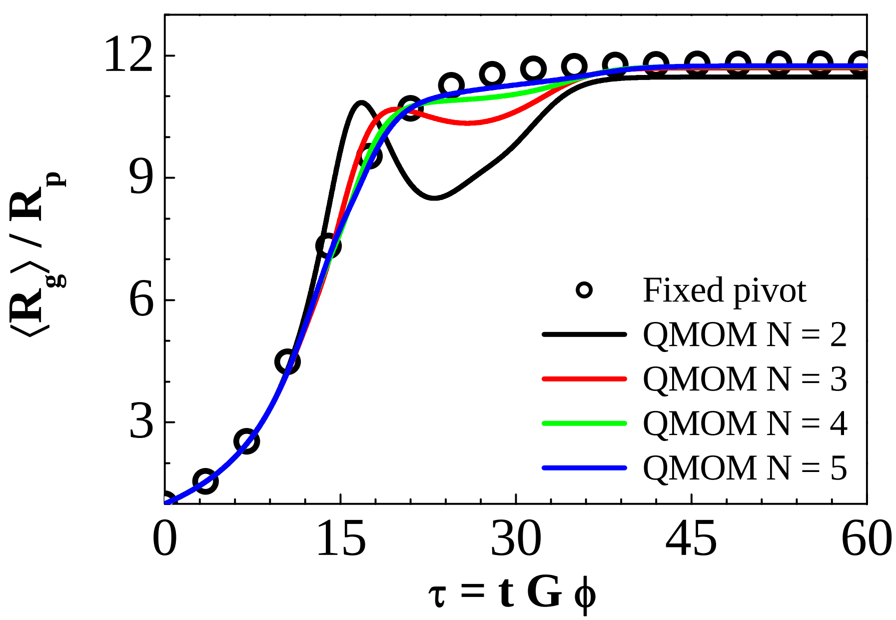
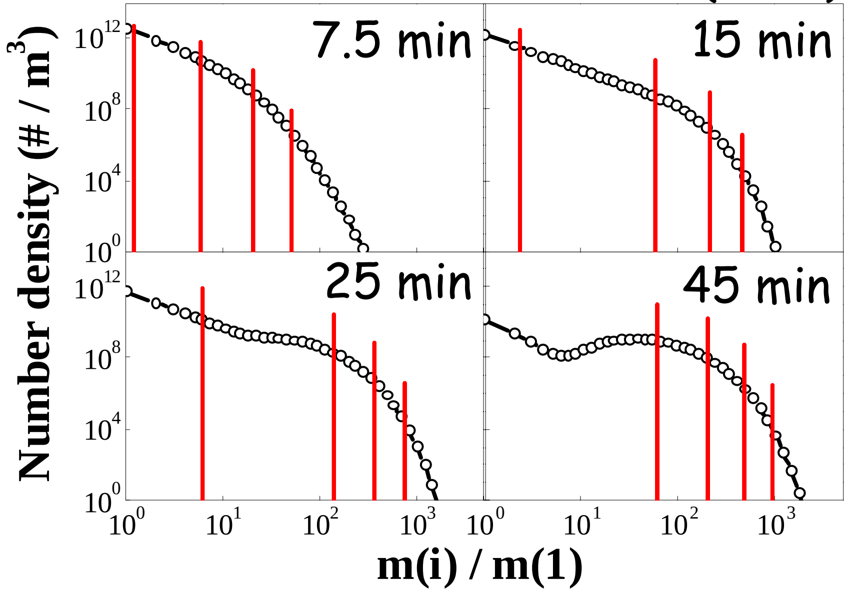


Cluster mass distribution (CMD)



Quadrature Method Of Moments (QMOM)

$$\frac{\partial m_k(\mathbf{x},t)}{\partial t} + \frac{\partial}{\partial x_i}\left[\langle u_i\rangle m_k(\mathbf{x},t)\right] - \frac{\partial}{\partial x_i}\left[D_t \frac{\partial m_k(\mathbf{x},t)}{\partial x_i}\right] =$$

$$\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} K_{i,j}^{A}\left[\left(\xi_i+\xi_j\right)^k - \xi_i^k - \xi_j^k\right] w_i w_j + \sum_{i=1}^{N} K_i^B \bar{b}_i^{(k)} w_i - \sum_{i=1}^{N} K_i^B \xi_i^k w_i$$

quadrature approximation

$$m_k = \int_0^\infty n(\xi)\, \xi^k \mathrm{d}\xi \approx \sum_{i=1}^{N} w_i \xi_i^k$$

Weights w_i and abscissas ξ_i calculated by PD algorithm

- Steady state is accurately modeled with two nodes ($N = 2$)
- For lower fractal dimensions ($d_f \leq 2$) larger number of nodes ($N = 4 - 5$) needed to be used

Estimation of model parameters from experiment

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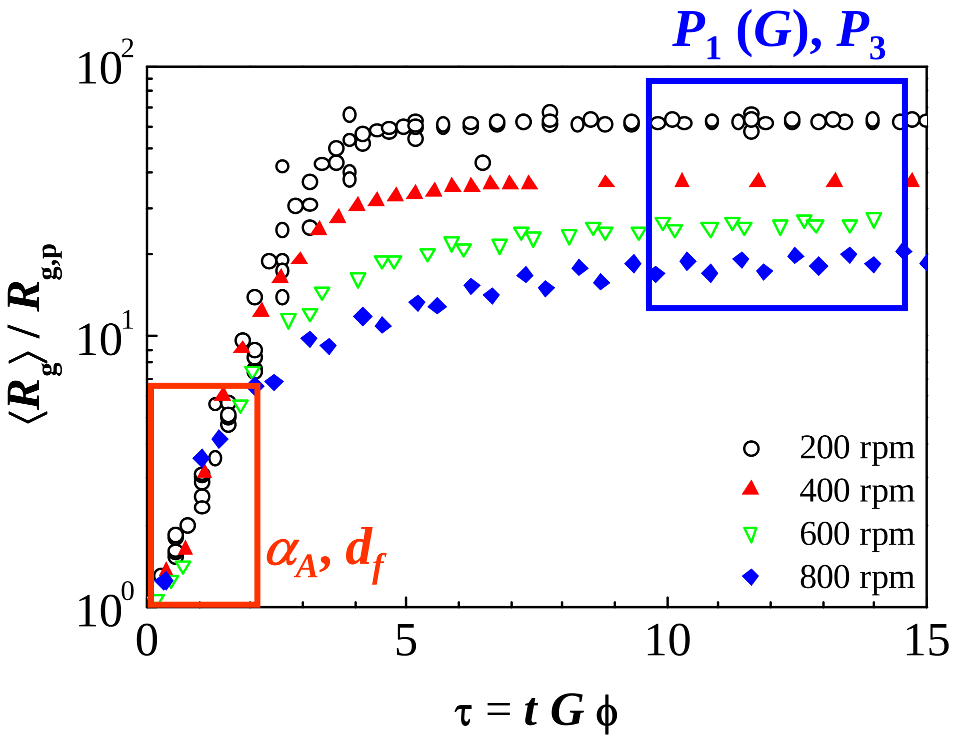
Dimensionless form of PBE

$$\frac{d\,x_k(\tau)}{d\tau} = \frac{1}{2}\sum_{i+j=k}\frac{K_{ij}^A}{V_0 G}x_i(\tau)x_j(\tau) - x_k(\tau)\sum_{i=1}^{\infty}\frac{K_{ik}^A}{V_0 G}x_i(\tau) + \sum_{m=k+1}^{\infty}\frac{\Gamma_{mk}K_m^B}{\phi_0 G}x_m(\tau) - \frac{K_k^B}{\phi_0 G}x_k(\tau)$$

$$x_i(\tau) = \frac{N_i(\tau)V_0}{\phi_0} \qquad \tau = t\,G\,\phi_0$$



Aggregation is linearly dependent on G

$$K^A_{\xi,\xi'} = \alpha_A G\left(\xi^{1/d_f} + \xi'^{1/d_f}\right)^3$$

Breakage is nonlinearly dependent on G

$$K^B_{\xi} = P_1(G)\left(\xi^{1/d_f}\right)^{P_3}$$

$R_P = 1.085\ \mu m$

$\phi_0 = 5 \times 10^{-5}$

$\alpha_A = 0.2$

$d_f = 2.1$

$P_1 = 1.551 \times 10^{12}\ G^{2.82}$

$P_3 = 4$

Dynamics of the system – full CFD (TC)

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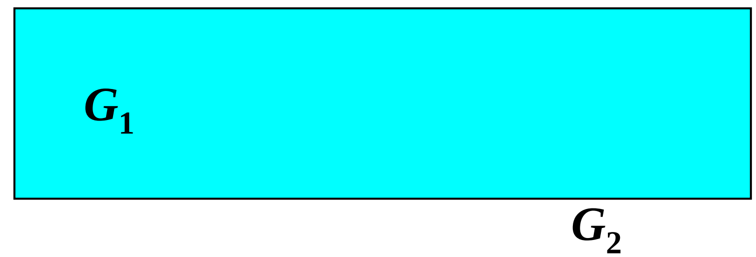
Taylor-Couette apparatus, 2D simulation, RSM of turbulence

Lumped model (often used in literature):

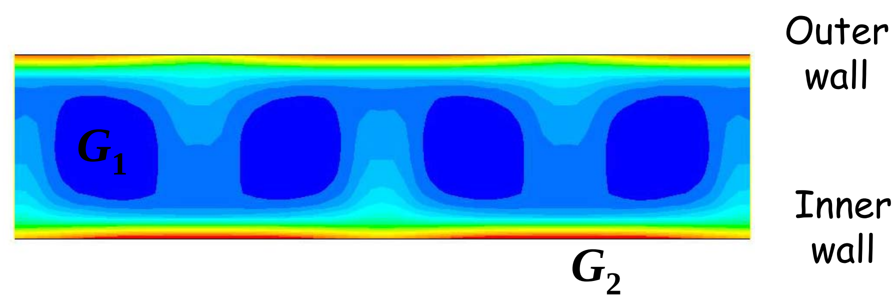
- particle distribution homogeneous
- shear rate is everywhere equal to the $\langle G \rangle$

$$G_1 = G_2 = G_i = \langle G \rangle$$



CFD model:

- particle distribution heterogeneous
- shear rate distribution heterogeneous



Homogeneous model:

- particle distribution homogeneous
- shear rate distribution heterogeneous

  breakage kernels properly averaged over volume

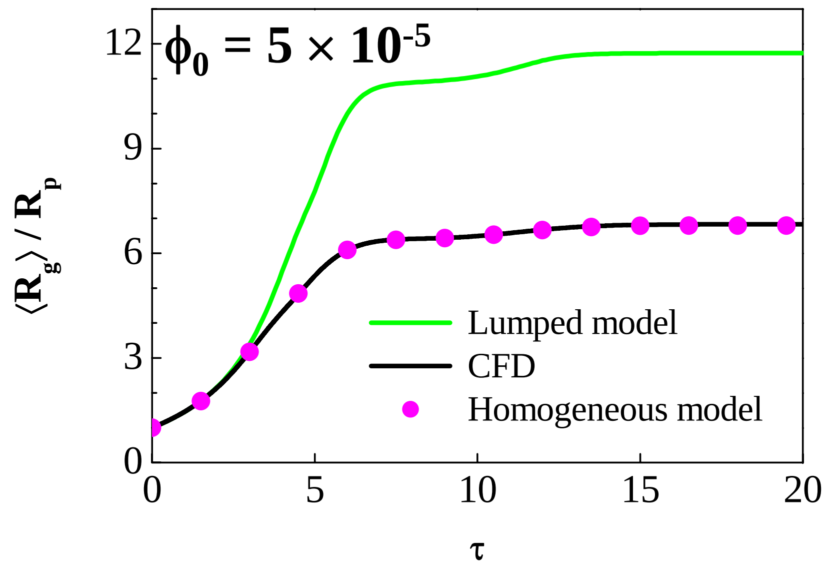
$$\langle G \rangle^{P_2} \neq \langle G^{P_2} \rangle$$

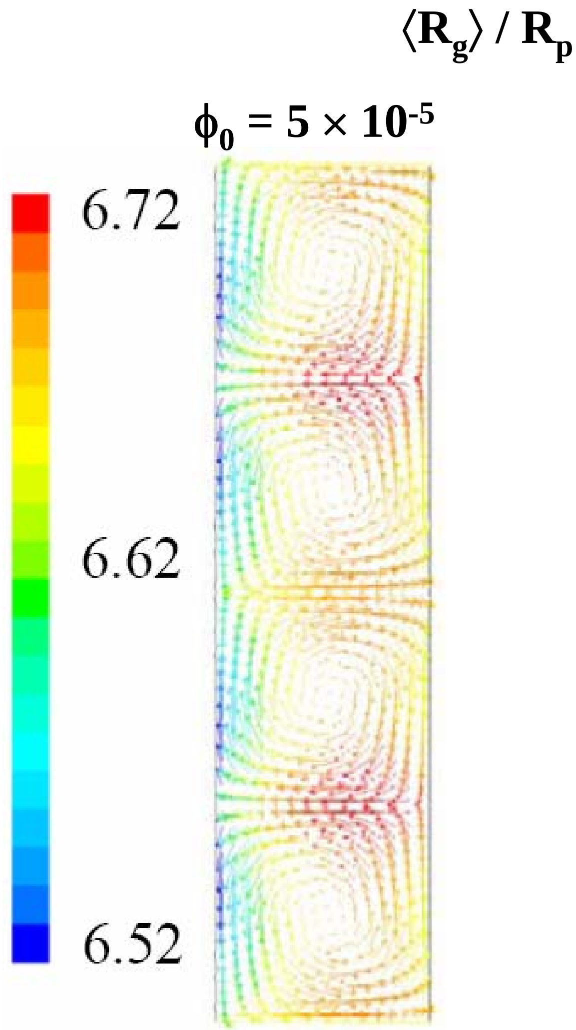
$$G_1 \neq G_2 \neq G_i \neq \langle G \rangle$$

Is the effect of spatial shear rate heterogeneity significant ?

$$G = \left(\frac{\varepsilon}{\nu} \right)^{1/2}$$

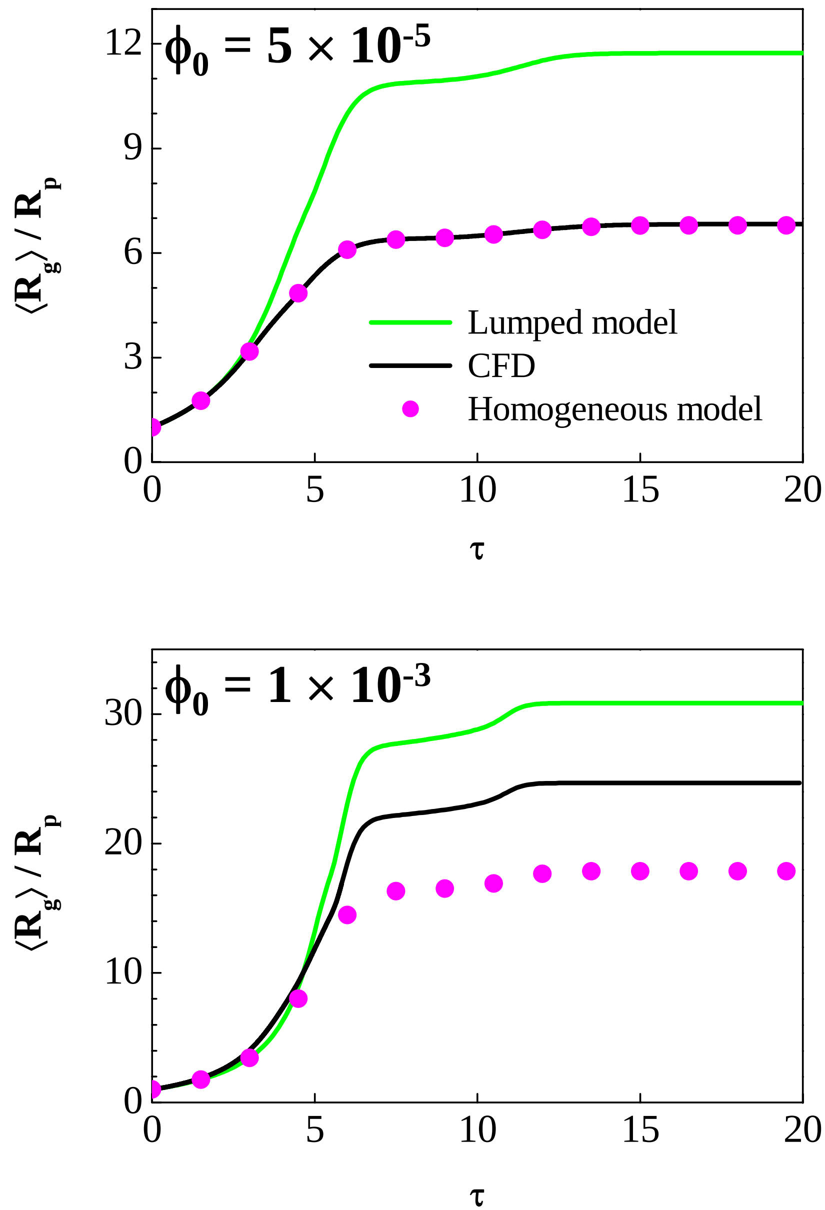
Dynamics of the system – full CFD (TC)

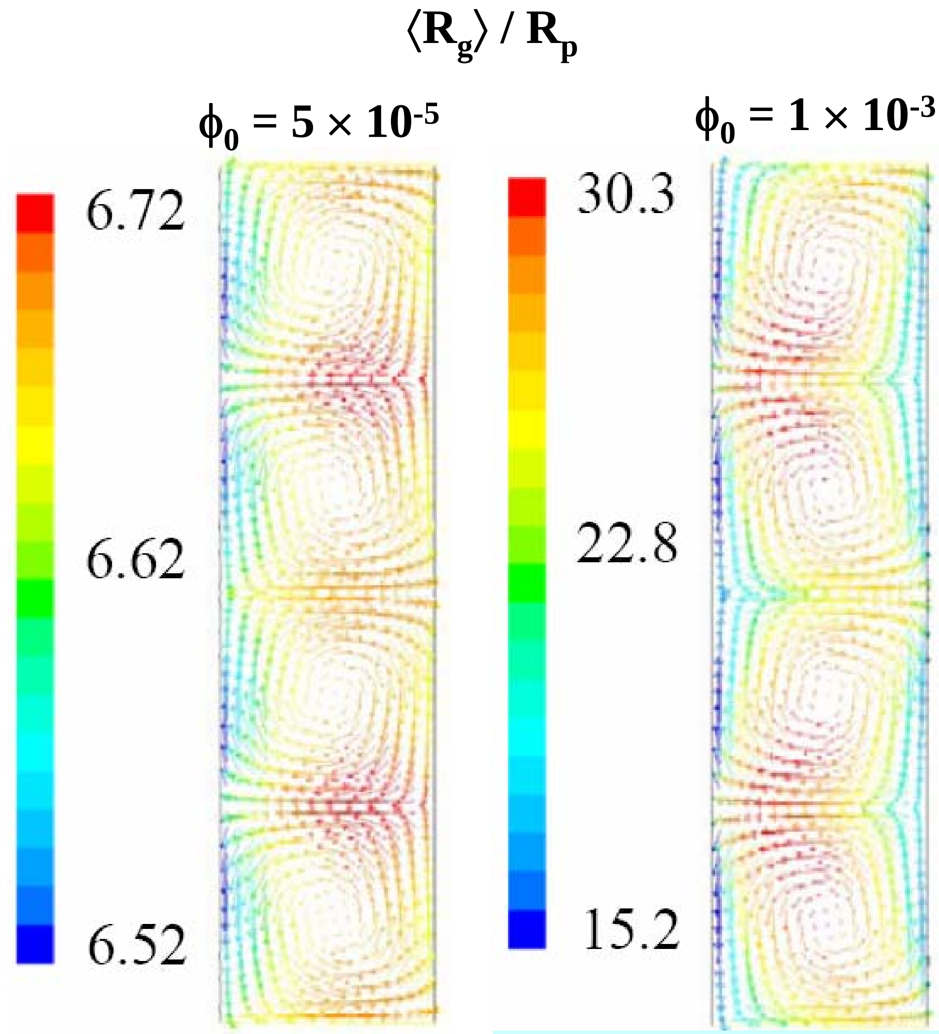




Assumption about particle distribution homogeneity is valid

Dynamics of the system – full CFD (TC)

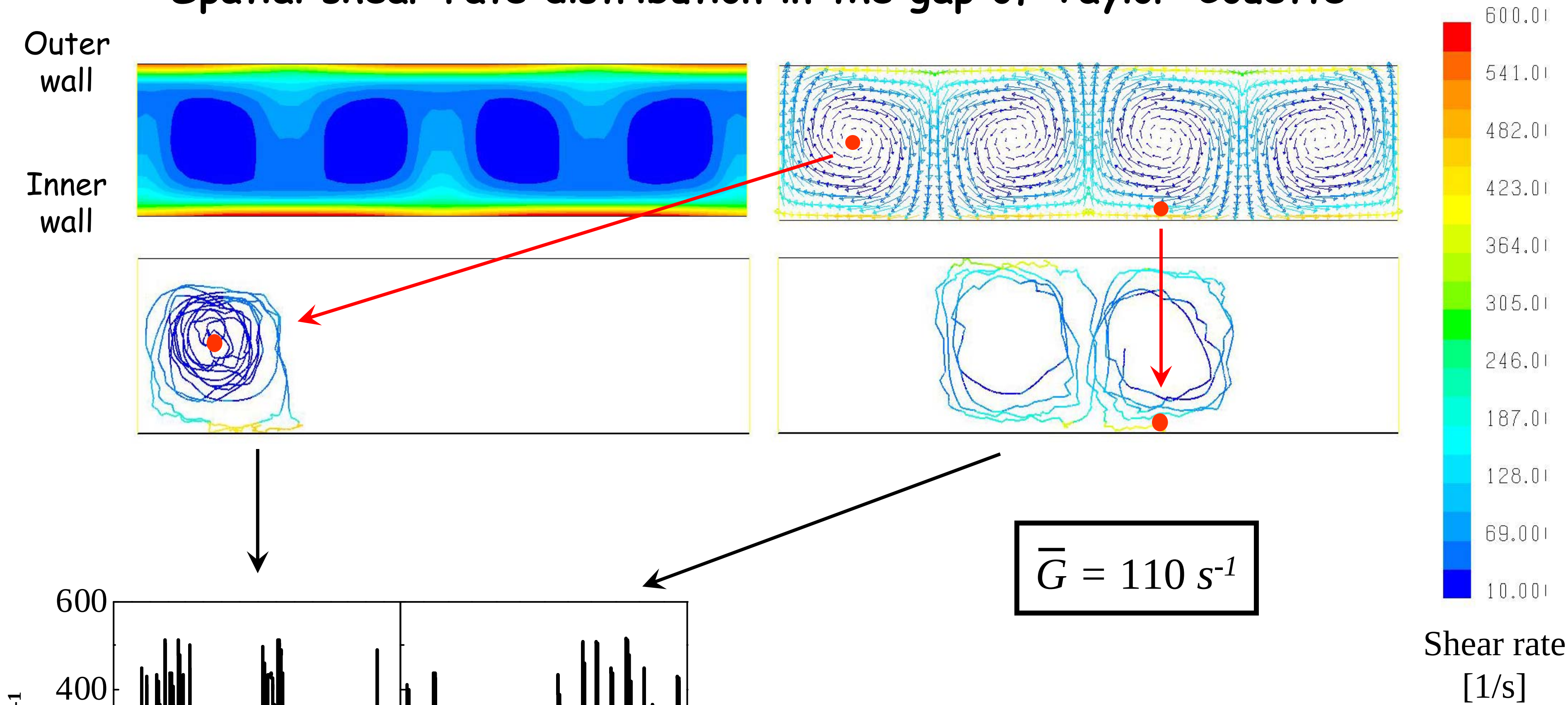


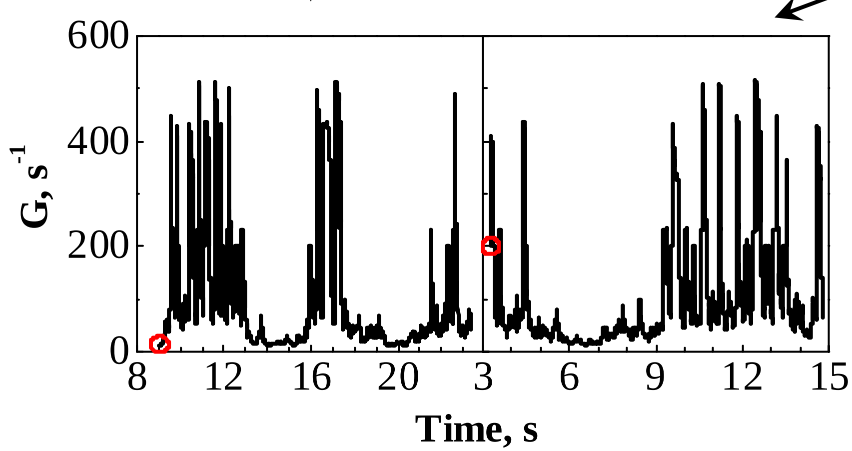


Assumption about particle distribution homogeneity is **NOT** valid

Fluid element trajectories

Spatial shear rate distribution in the gap of Taylor-Couette





Two examples of fluid element trajectories corresponding to the starting point from low and high shear rate value

Fluid element tracking – Process timescales

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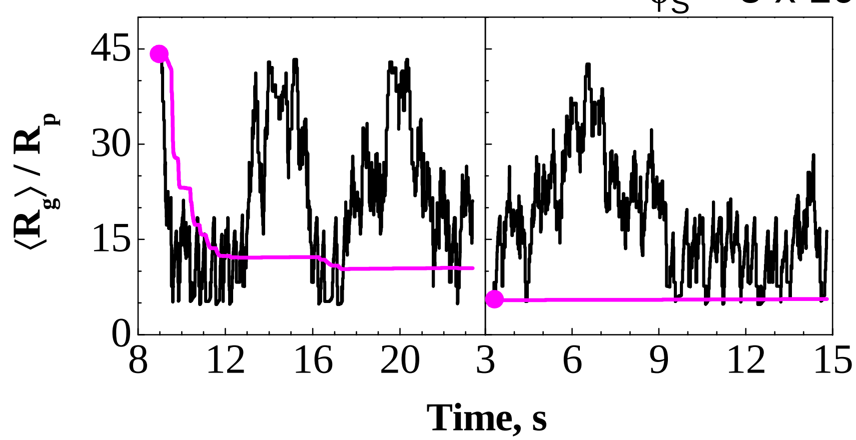
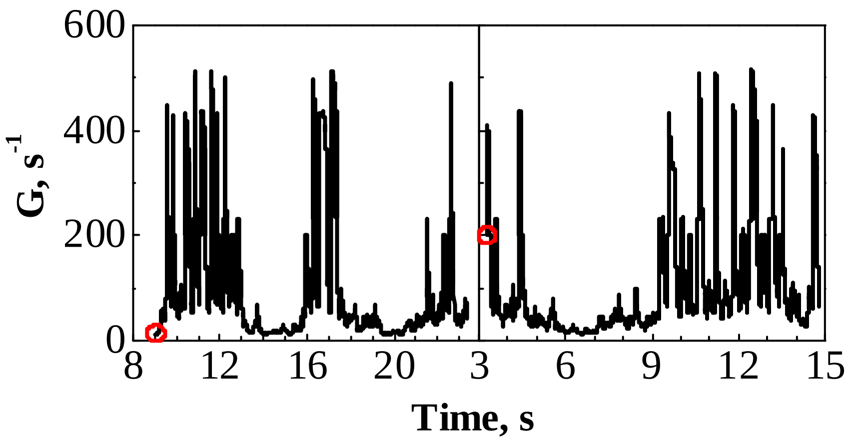
Macro-mixing: $\tau_M = \frac{k}{\varepsilon}$ ← **k, ε** (CFD) → $G = \left(\frac{\varepsilon}{\nu}\right)^{1/2}$ → **Aggregation / breakage at steady state:**

$$\tau_A = \frac{1}{K^A\left(G;\langle R_g\rangle,\langle R_g\rangle\right)N} \qquad \tau_B = \frac{1}{K^B\left(G;\langle R_g\rangle\right)}$$

$\tau_A, \tau_B \gg \tau_M$

$\phi_S = 5 \times 10^{-5}$





Homogeneous model:

- particle distribution homogeneous
- aggregation / breakage kernels properly averaged over volume

$$\bar{K}^A_{\xi,\xi'} = \frac{1}{V}\int_V K^A_{\xi,\xi'}(G)\mathrm{dV} \qquad \bar{K}^B_{\xi} = \frac{1}{V}\int_V K^B_{\xi}(G)\mathrm{dV}$$

Shear rate history

Calculation starts from the steady state distribution corresponding to the starting point of shear rate

Fluid element tracking – Process timescales

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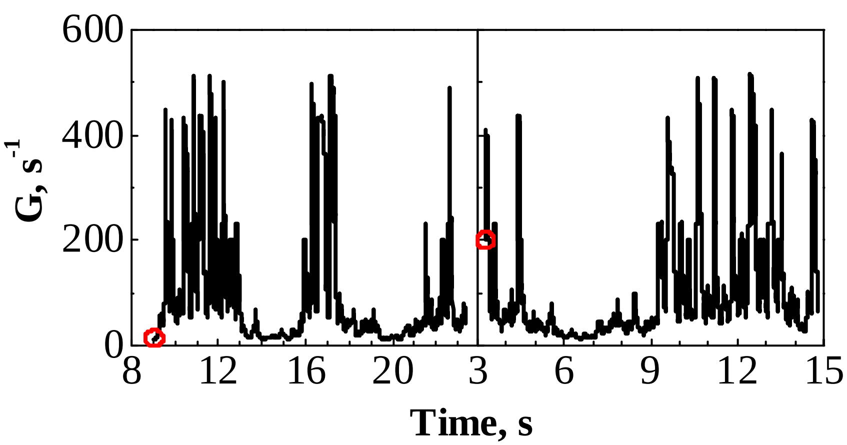
$$\tau_A = \frac{1}{K^A\left(G;\langle R_g\rangle,\langle R_g\rangle\right)N} \qquad \tau_B = \frac{1}{K^B\left(G;\langle R_g\rangle\right)}$$

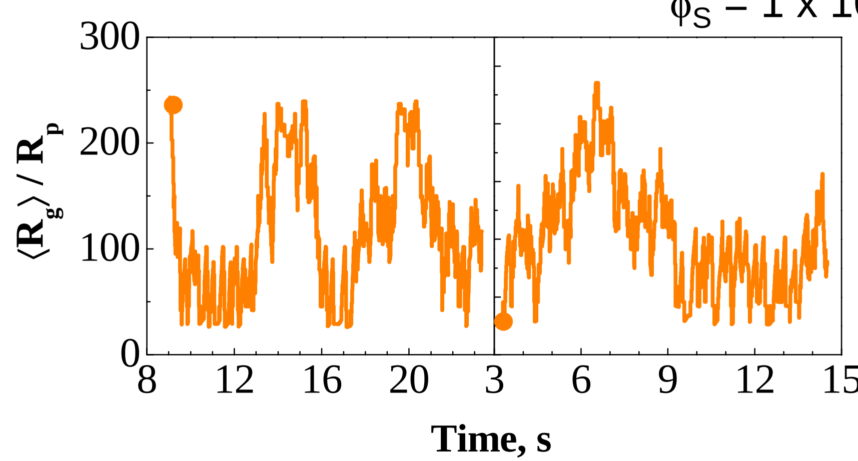


Shear rate history

Calculation starts from the steady state distribution corresponding to the starting point of shear rate

$\tau_A, \tau_B << \tau_M$

$\phi_S = 1 \times 10^{-2}$



Equilibrium model:

- particle distribution relaxes immediately to steady state according to local shear rate

Analysis of timescales – Conclusion

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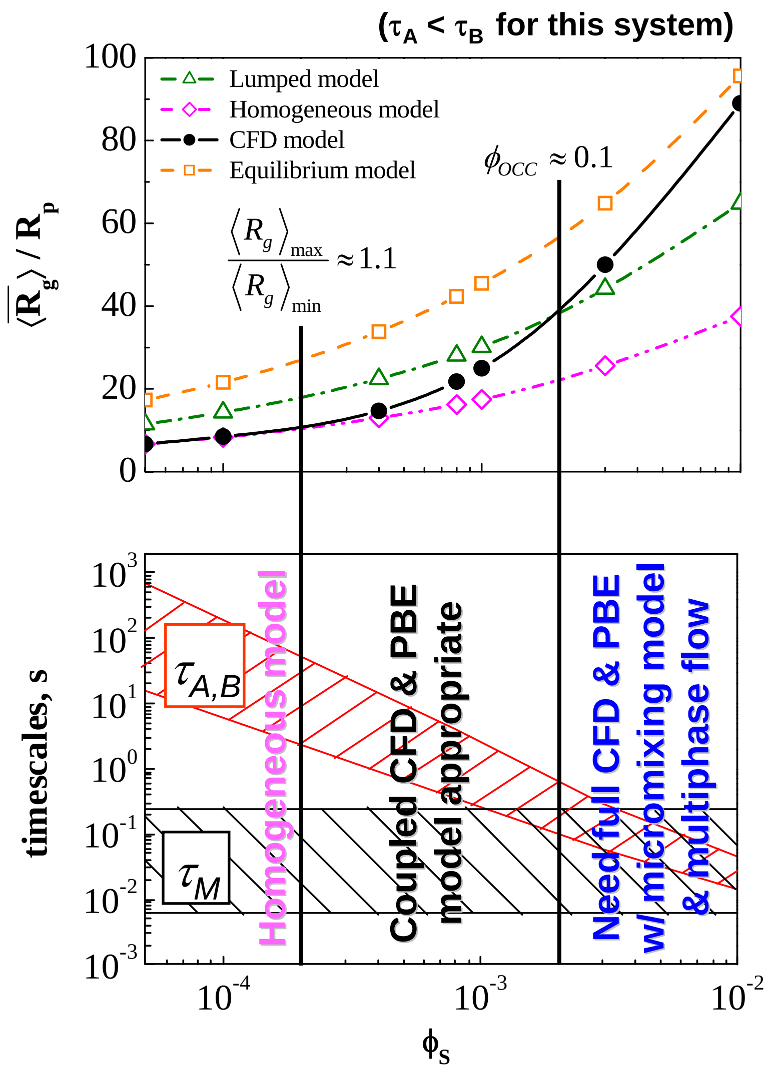

- Based on timescales analysis it is possible to decide which model is appropriate for certain conditions
- At low volume fraction (< 4 × 10^{-4}) CFD model can by efficiently replaced by homogeneous model
- Kinetic parameters obtained from lumped model are not applicable for different vessel geometry – **significant effect of shear rate heterogeneity**
- CFD + PBE need to be used already for rather mild solid volume fractions

Note: region of validity of homogeneous model in stirred tank is shifted to left compare to TC

Note: occupied volume fraction can be used to check significance of viscosity on flow field