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Slide of the Seminar

Restructuring of colloidal aggregates in turbulent flows

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Restructuring of colloidal aggregates in turbulent flows

Matthäus U. Bäbler
KTH Royal Institute of Technology, Stockholm, Sweden

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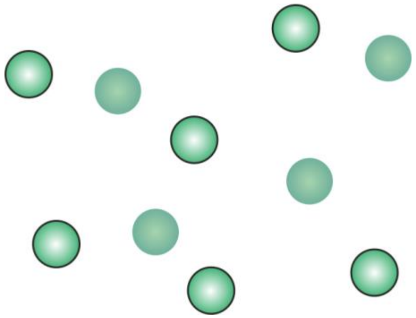
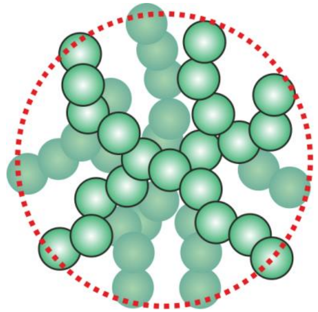
2014-04-15

Aggregation of small particles



Aggregation

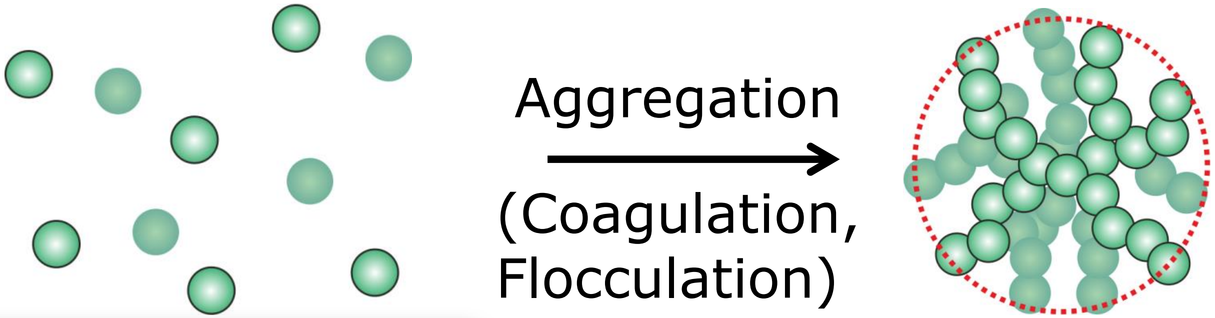
(Coagulation,
Flocculation)



Primary particles
~ (10 nm – 10 μm)

Aggregates
~ up to milimeters

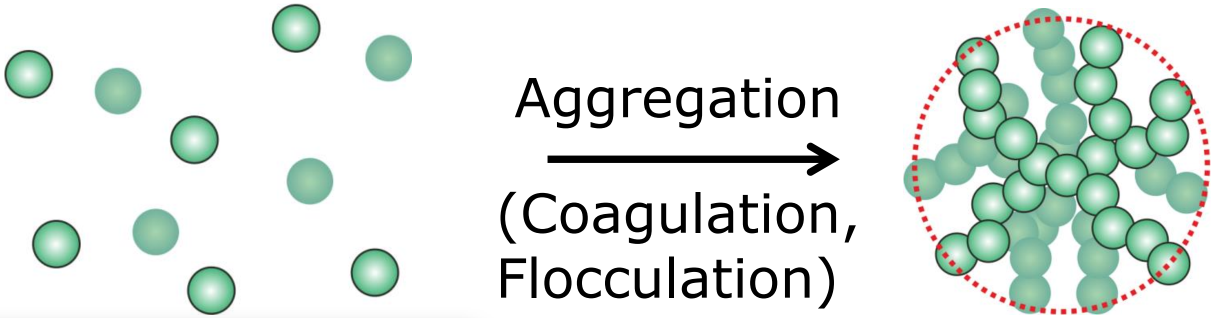
Aggregation of small particles



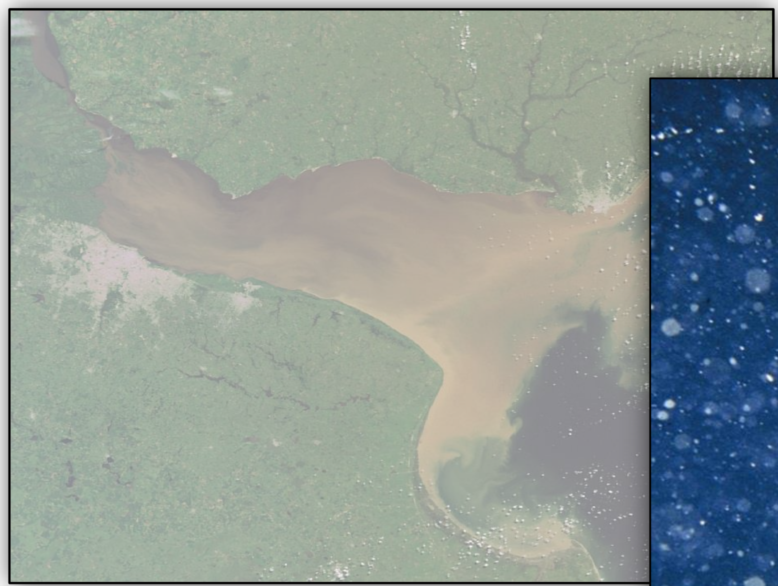
Aggregates
~ up to milimeters

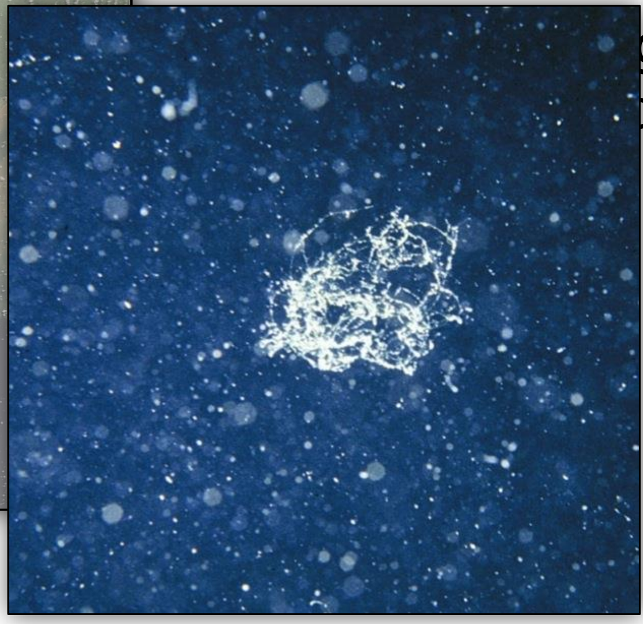
Picture: Satelite image Rio de la Plata Estuary, March 10, 2010 (www.eosnap.com, retrieved 2014-03-12),

Aggregation of small particles



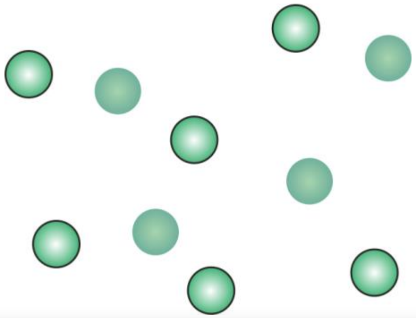
…gregates
…o milimeters





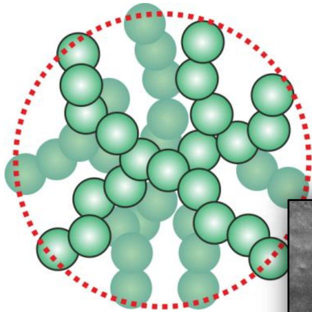
Picture: H. P. Grossart, IGB,
Leibniz-Institute of Freshwater
Ecology and Inland Fisheries

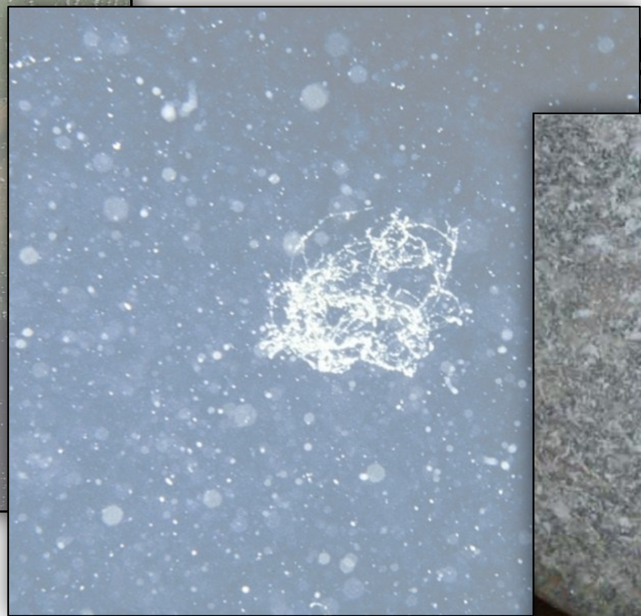
Aggregation of small particles



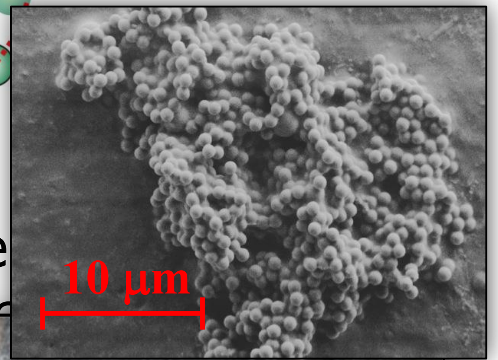
Aggregation

(Coagulation, Flocculation)



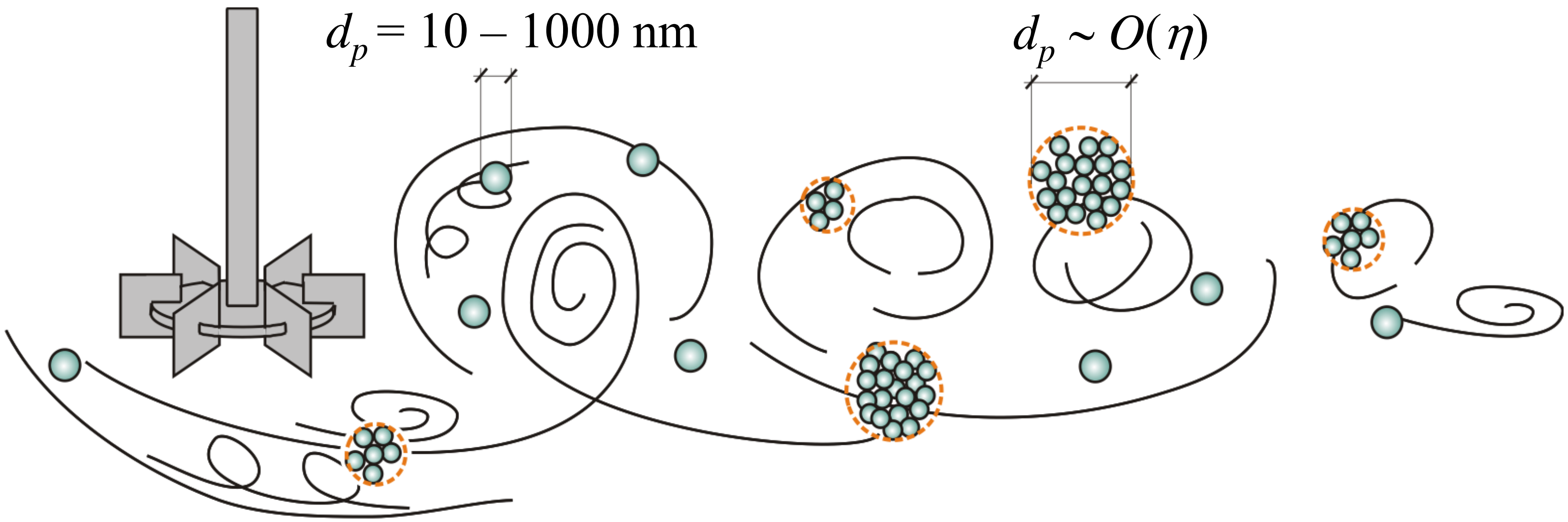


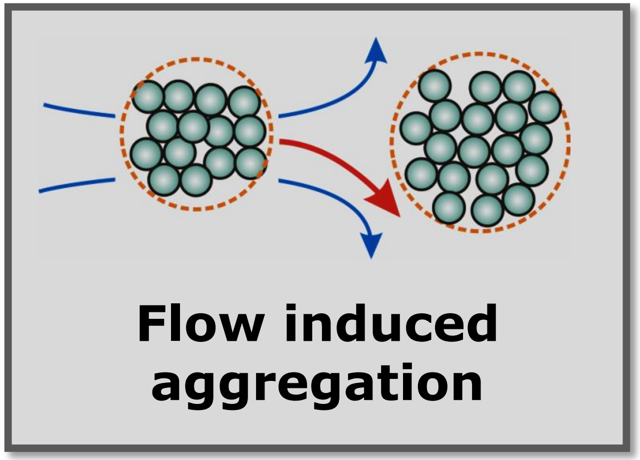
gregate

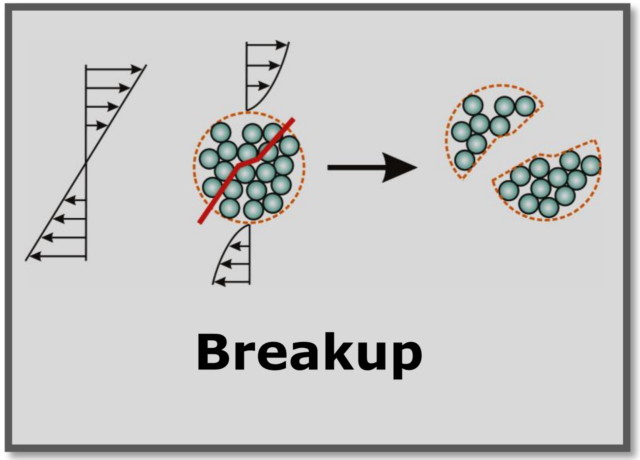


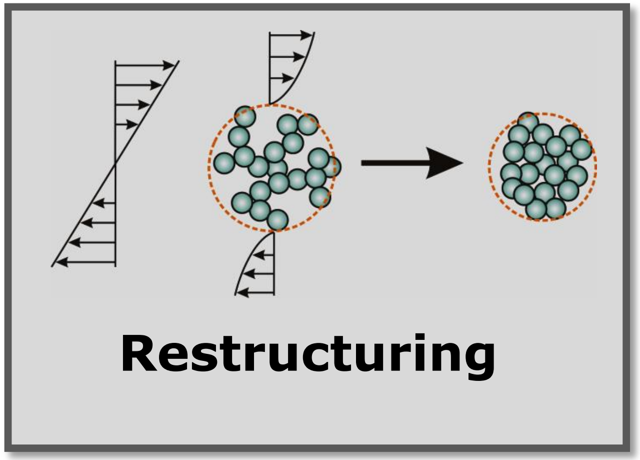
Pictures: M. Soos, D. Marchisio, J. Sefcik, *AIChE J.* (2013), *and* Soos et al., *J. Colloid Interface Sci.* (2008)

Aggregation of small particles

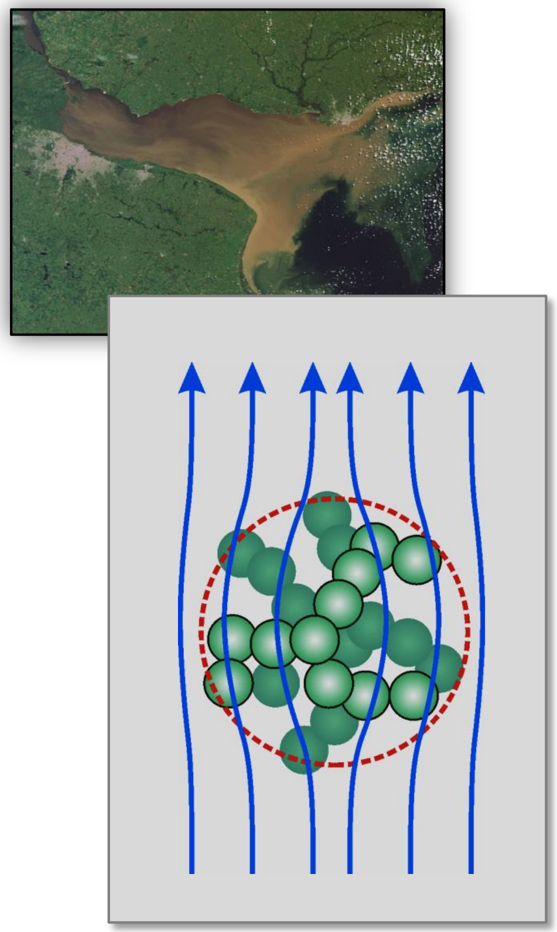




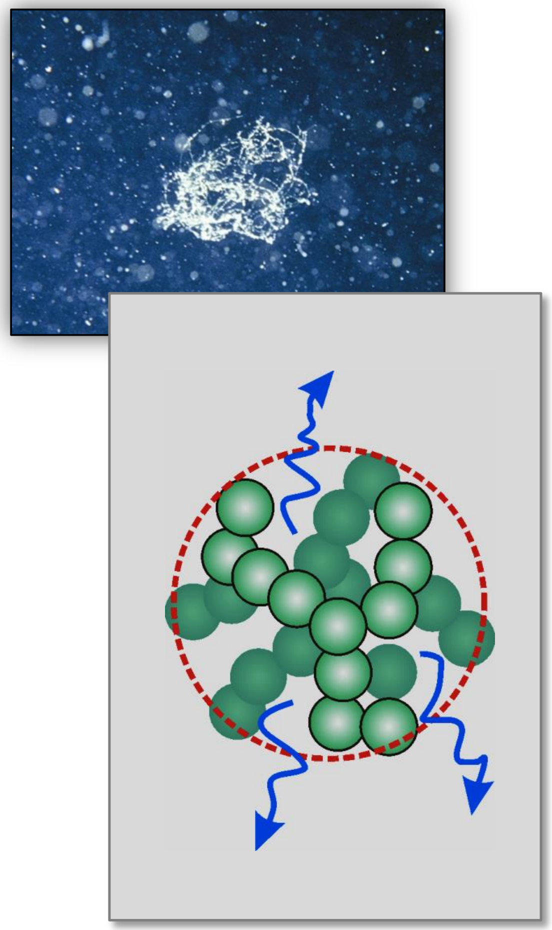




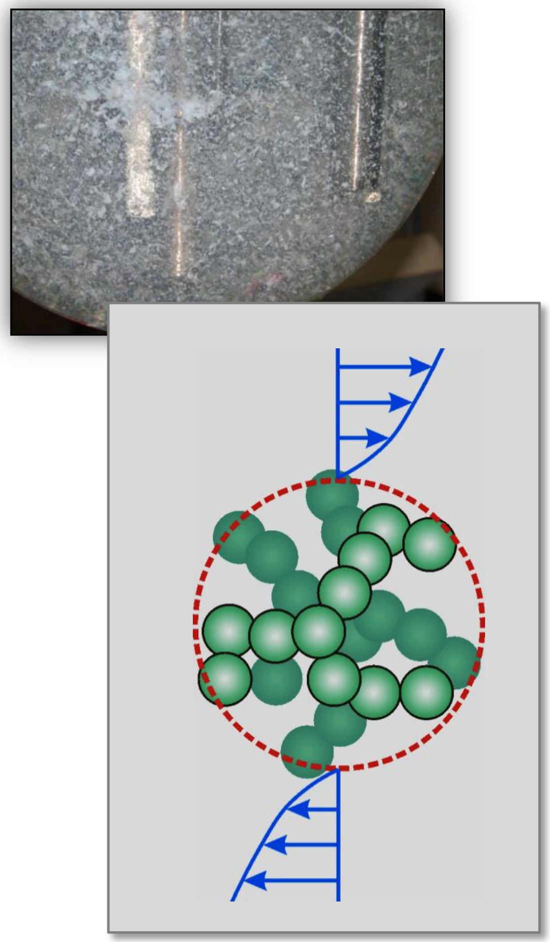
Structure and restructuring



Hydrodynamic drag
and settling velocity



Solute loading
(drugs, nutritions)



Mechanical
strength

ROYAL INSTITUTE OF TECHNOLOGY

Outline

- Introduction
- Structure of aggregates: aggregate fractal dimension
- Strategy for exploring restructuring
- Population balance model
- Breakup model
- Results
- Conclusions

Outline

- Introduction
- **Structure of aggregates: aggregate fractal dimension**
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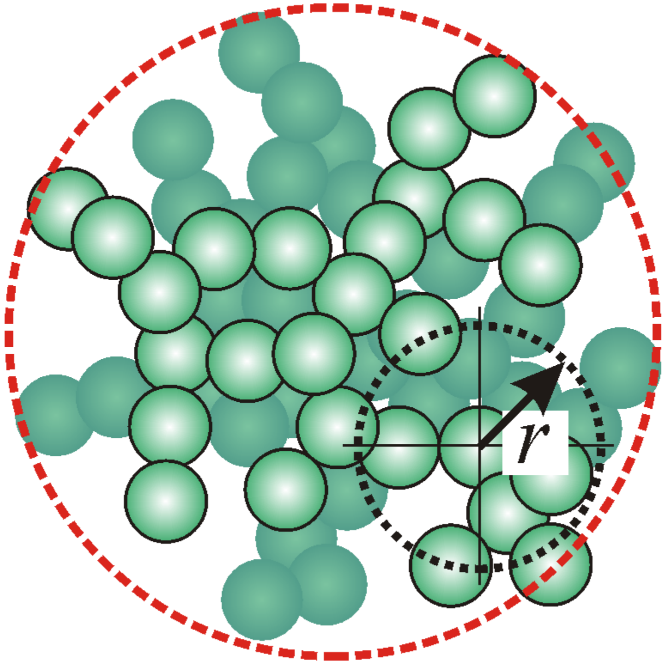
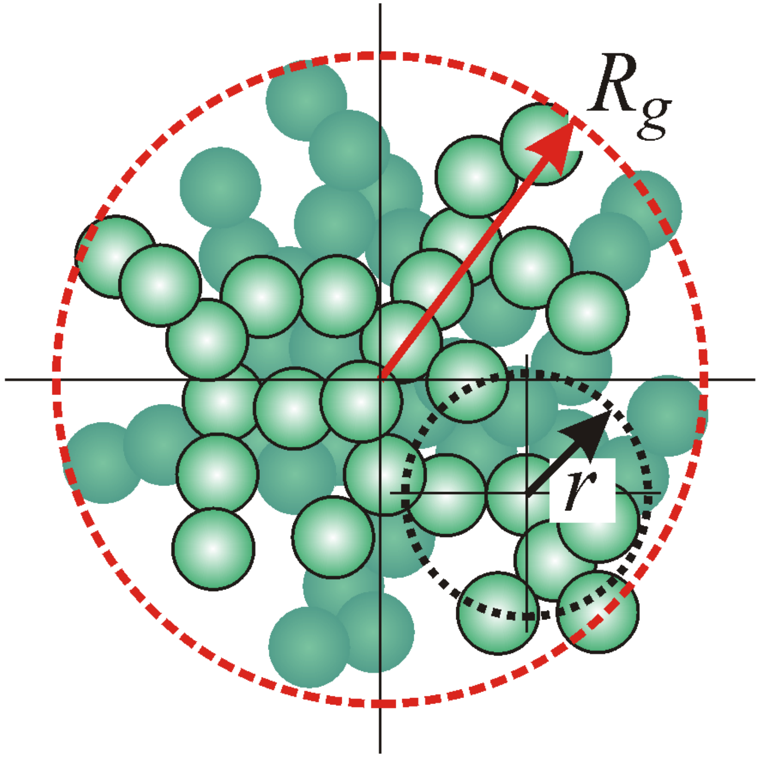
Aggregate fractal dimension



- Pair-correlation function

$$g(r) = \frac{\langle \rho(x)\rho(x+r) \rangle}{\langle \rho^2(x) \rangle} \sim r^{d_f - 3}$$

Aggregate fractal dimension



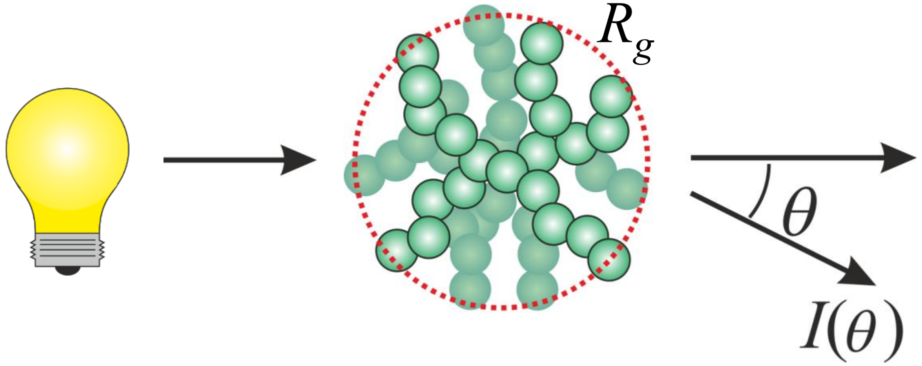
- Pair-correlation function

$$g(r) = \frac{\langle \rho(x)\rho(x+r)\rangle}{\langle \rho^2(x)\rangle} \sim r^{d_f-3}$$

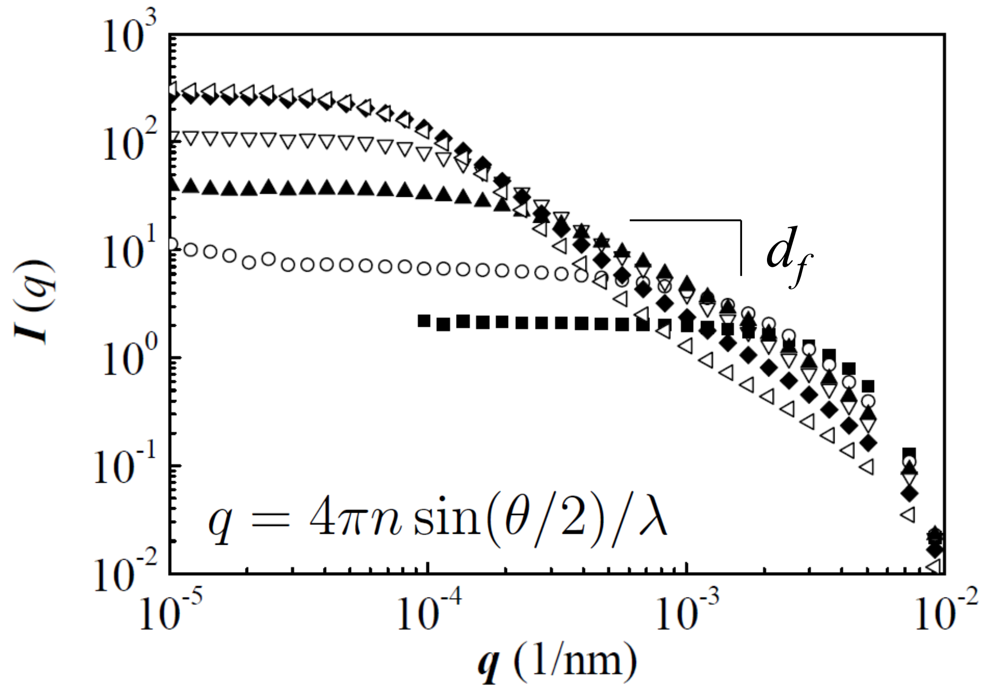
- Scaling of aggregate size

$$i \sim R_g^{d_f}$$

Measuring mass fractal dimension



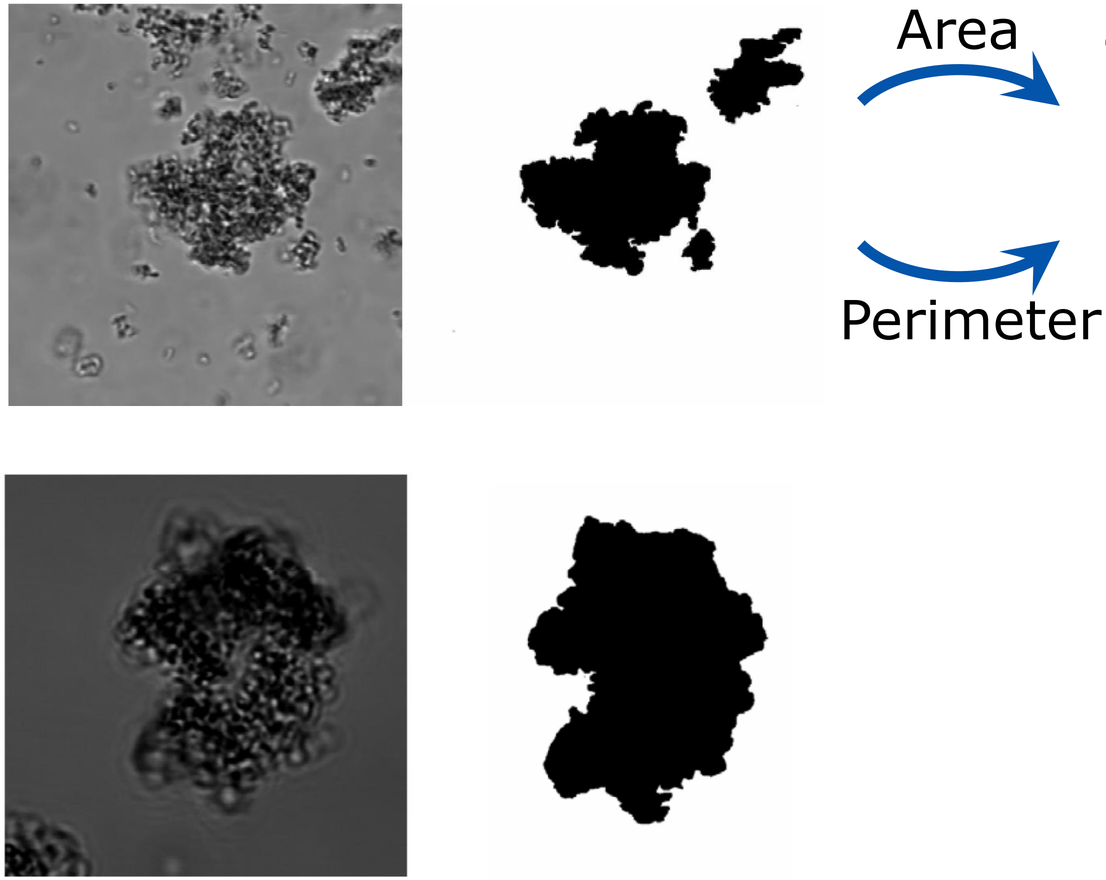
Static Light Scattering

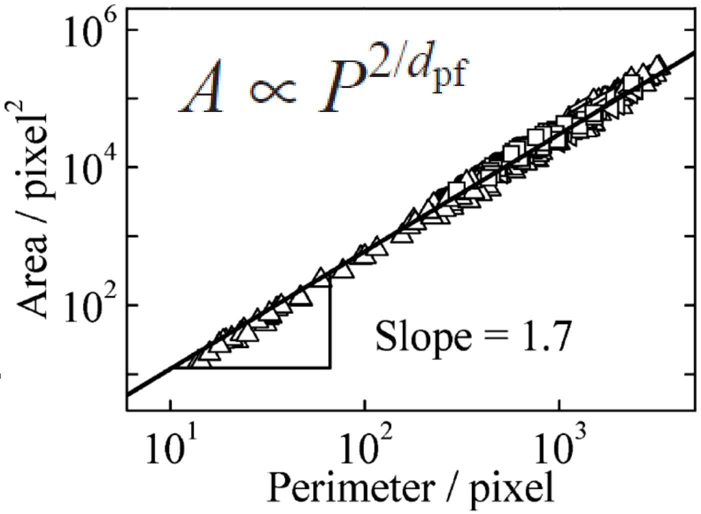


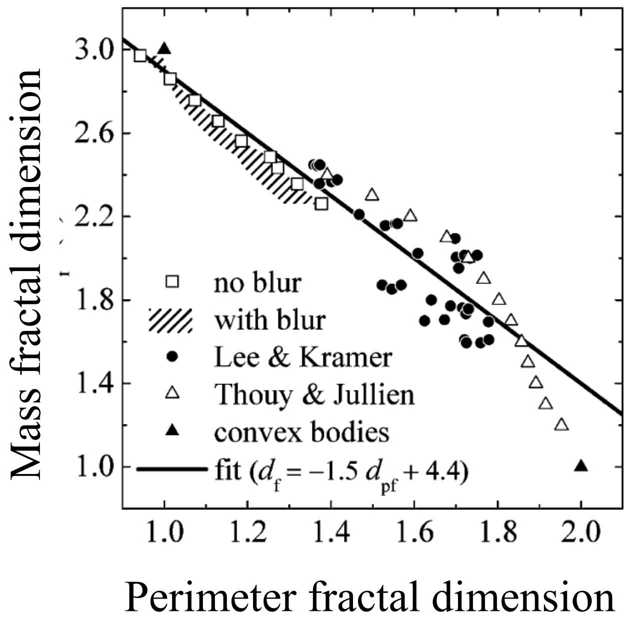
For $d_p \ll \lambda$ and not too dense aggregates:
d_f from the log-log slope

Moussa *et al.*, *Langmuir* (2007)

Measuring mass fractal dimension

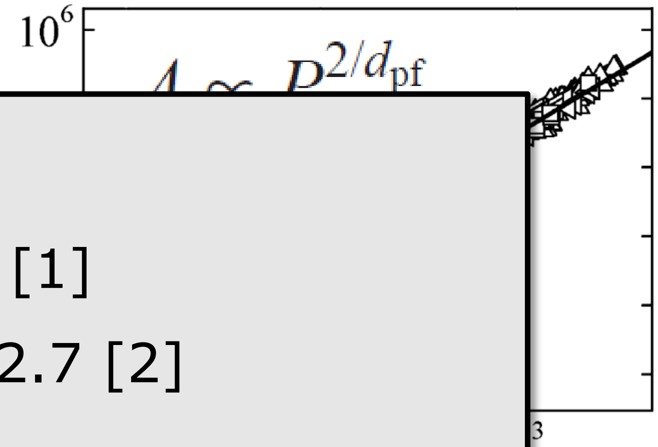






Left: A. S. Moussa, *PhD Thesis, ETH Zurich* (2008)
Upper right: Ehrl et al., Langmuir (2008), Lower right: Ehrl et al., J. Phys. Chem. B (2009)

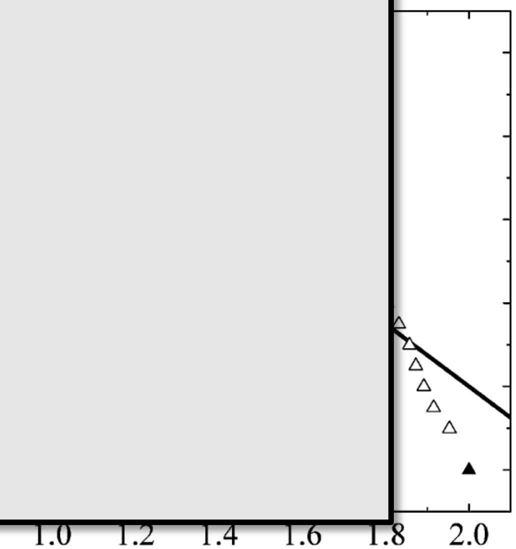
Measuring mass fractal dimension



In (turbulently) stirred fluids

- Early stages of aggregation $d_f \approx 2.1$ [1]
- Late stages of aggreagtion $d_f \approx 2.3\text{-}2.7$ [2]

[1] Babler, et al., Langmuir (2010), [2] Soos et al., J. Colloid Interface Sci. (2007)



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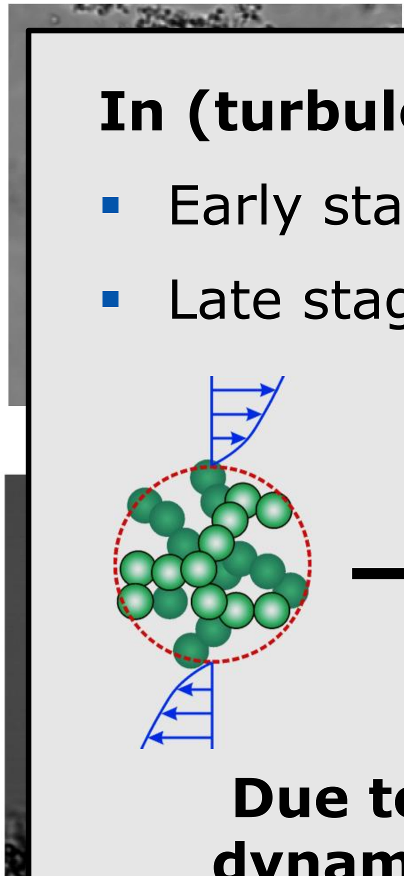
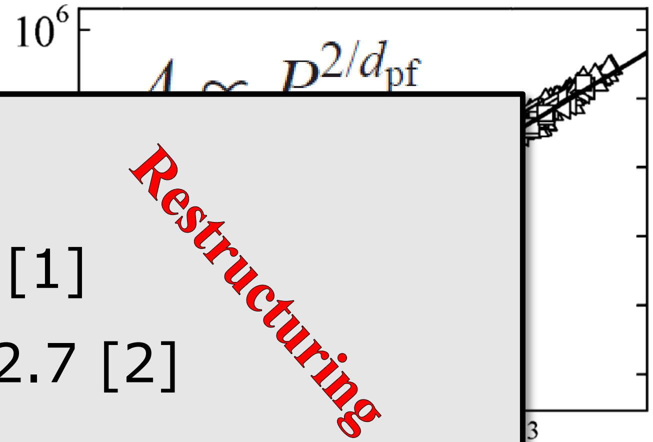
Measuring mass fractal dimension





In (turbulently) stirred fluids

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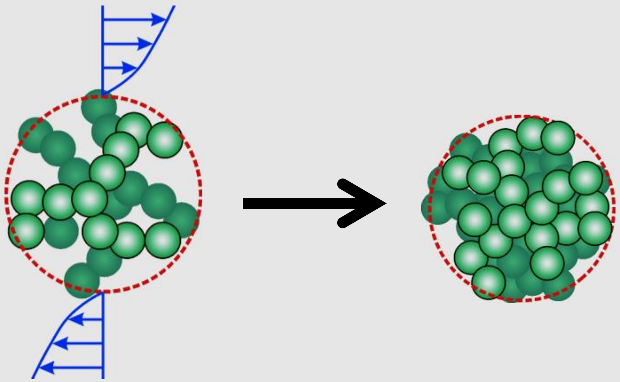
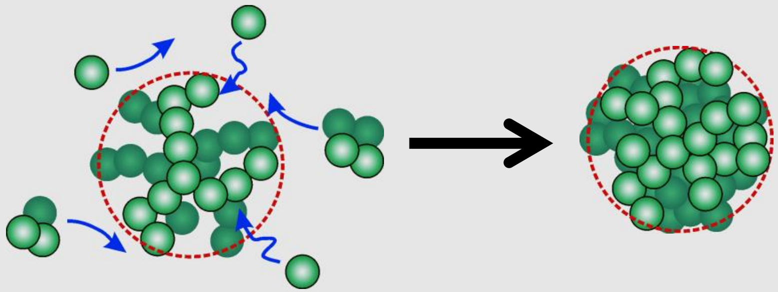
Restructuring

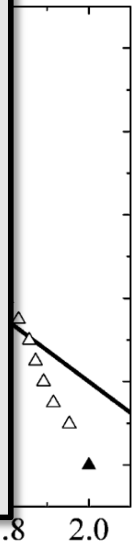


Due to hydro-dynamic stress



Due to particle-cluster aggregation

[1] Babler, et al., Langmuir (2010), [2] Soos et al., J. Colloid Interface Sci. (2007)



Left: A. S. Moussa, *PhD Thesis, ETH Zurich* (2008)
Upper right: Ehrl et al., Langmuir (2008), Lower right: Ehrl et al., J. Phys. Chem. B (2009)

Alternative approach

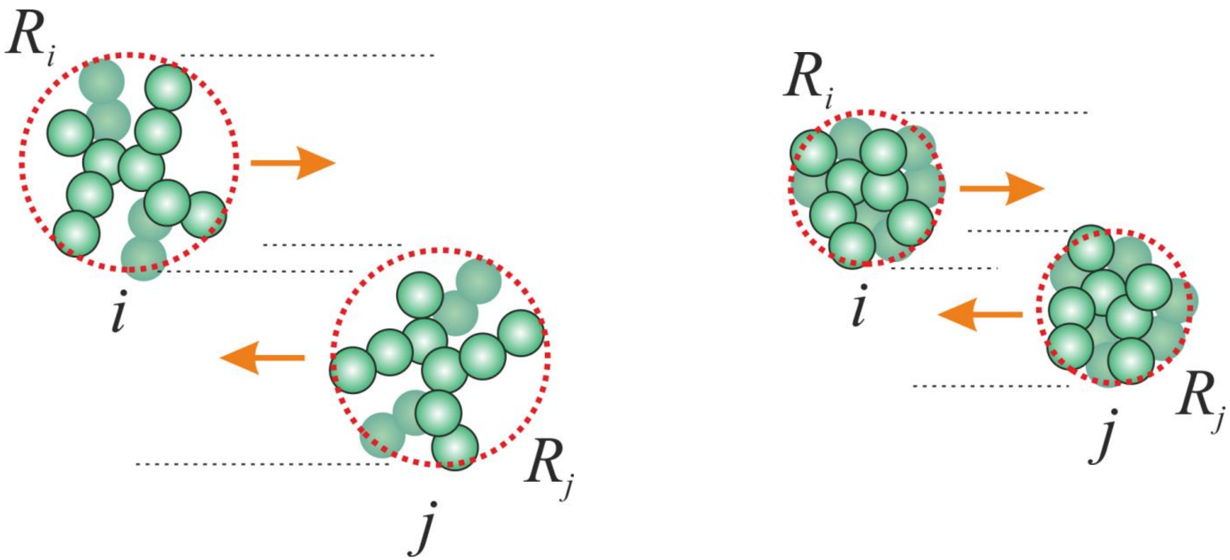
Consider an aggregate i colliding with an aggregate j

i, j = number of primary particle per aggregate

$$i \sim R_g^{d_f}$$

Open aggregate
Small d_f

Dense aggregates
large d_f



$$K_{ij} \sim \left(R_i + R_j\right)^3 \sim \left(i^{1/d_f} + j^{1/d_f}\right)^3$$

⇨ d_f can be estimated from measuring the aggregation rate

Babler *et al.*, *Langmuir* (2010)

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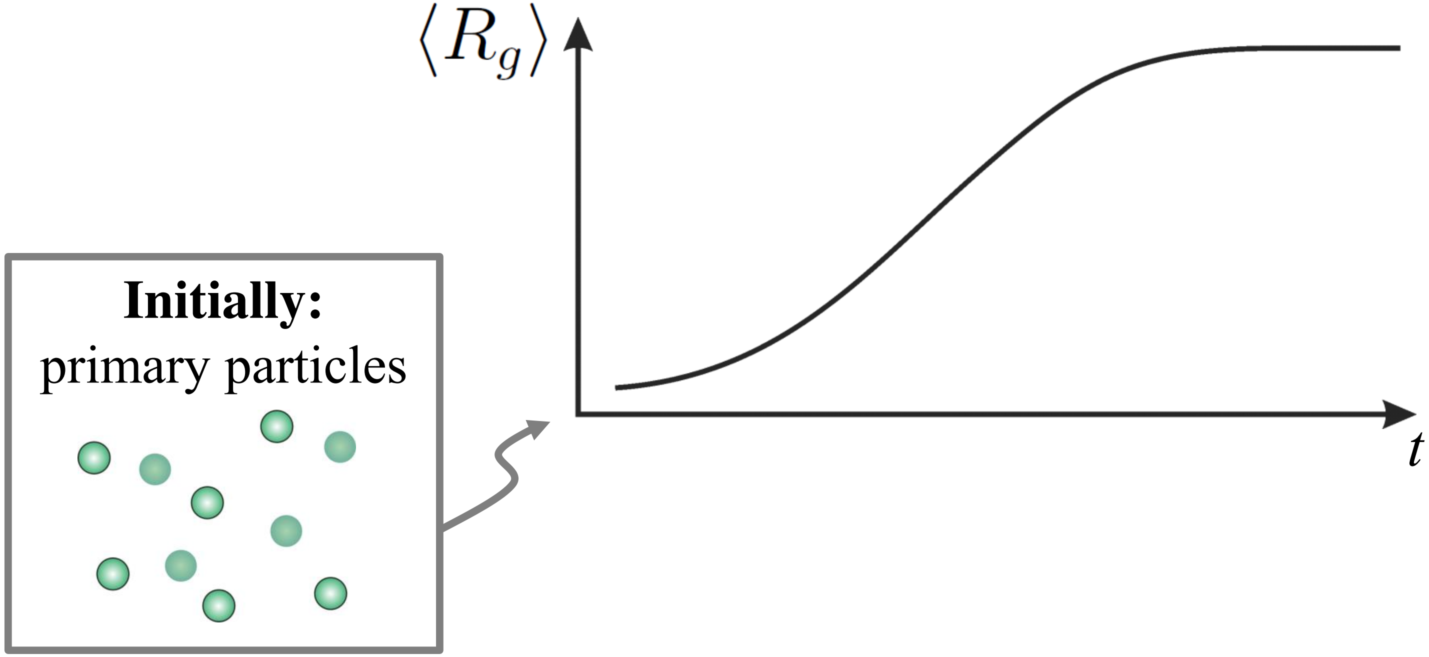
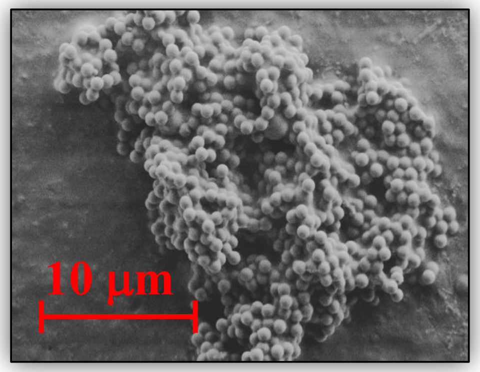
Strategy pursued

Exploring restructuring during aggregation of primary particles





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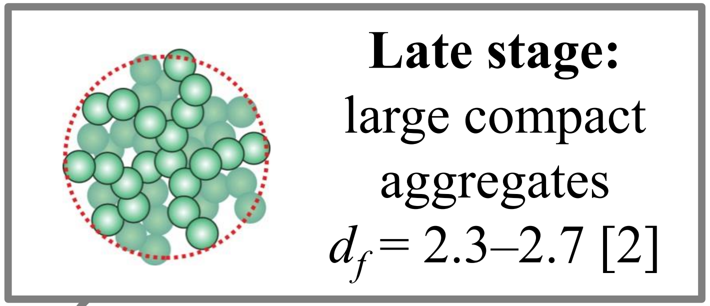

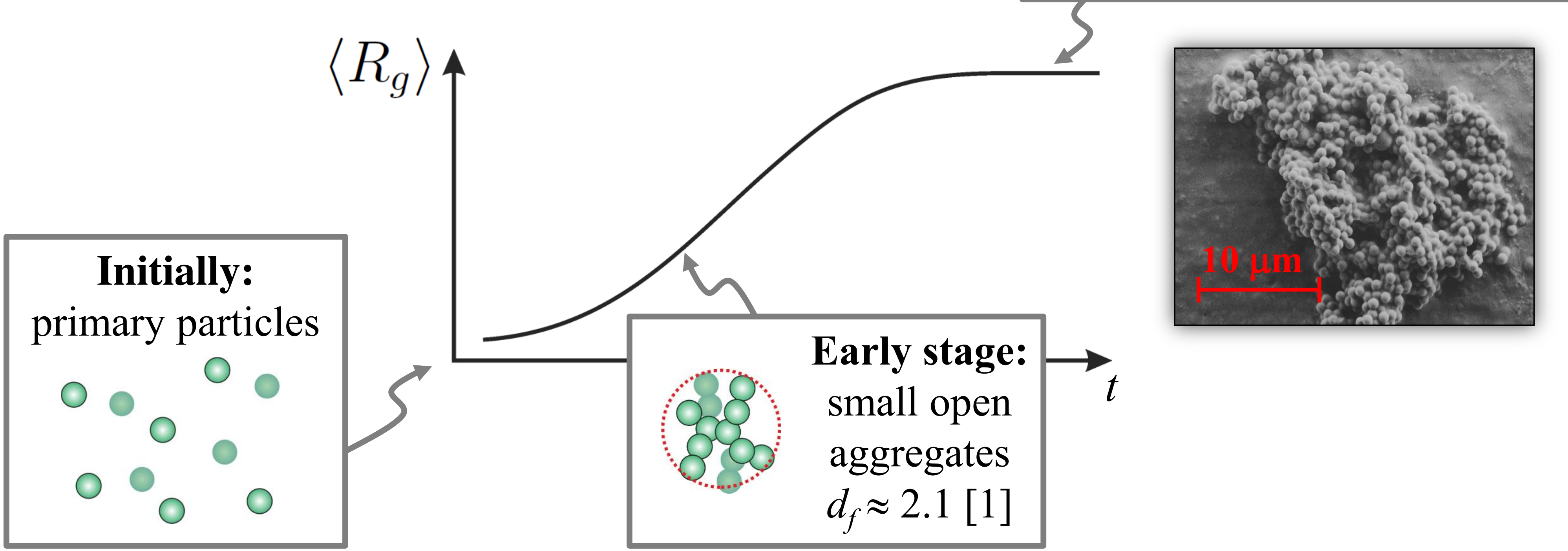

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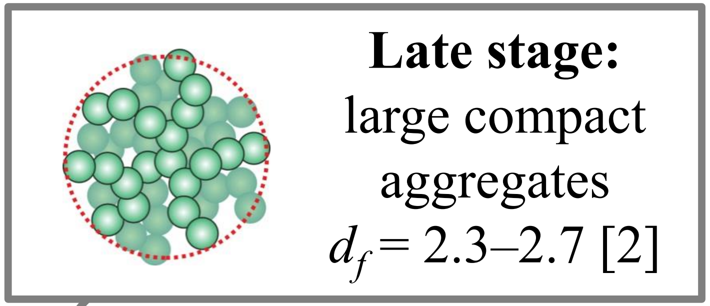
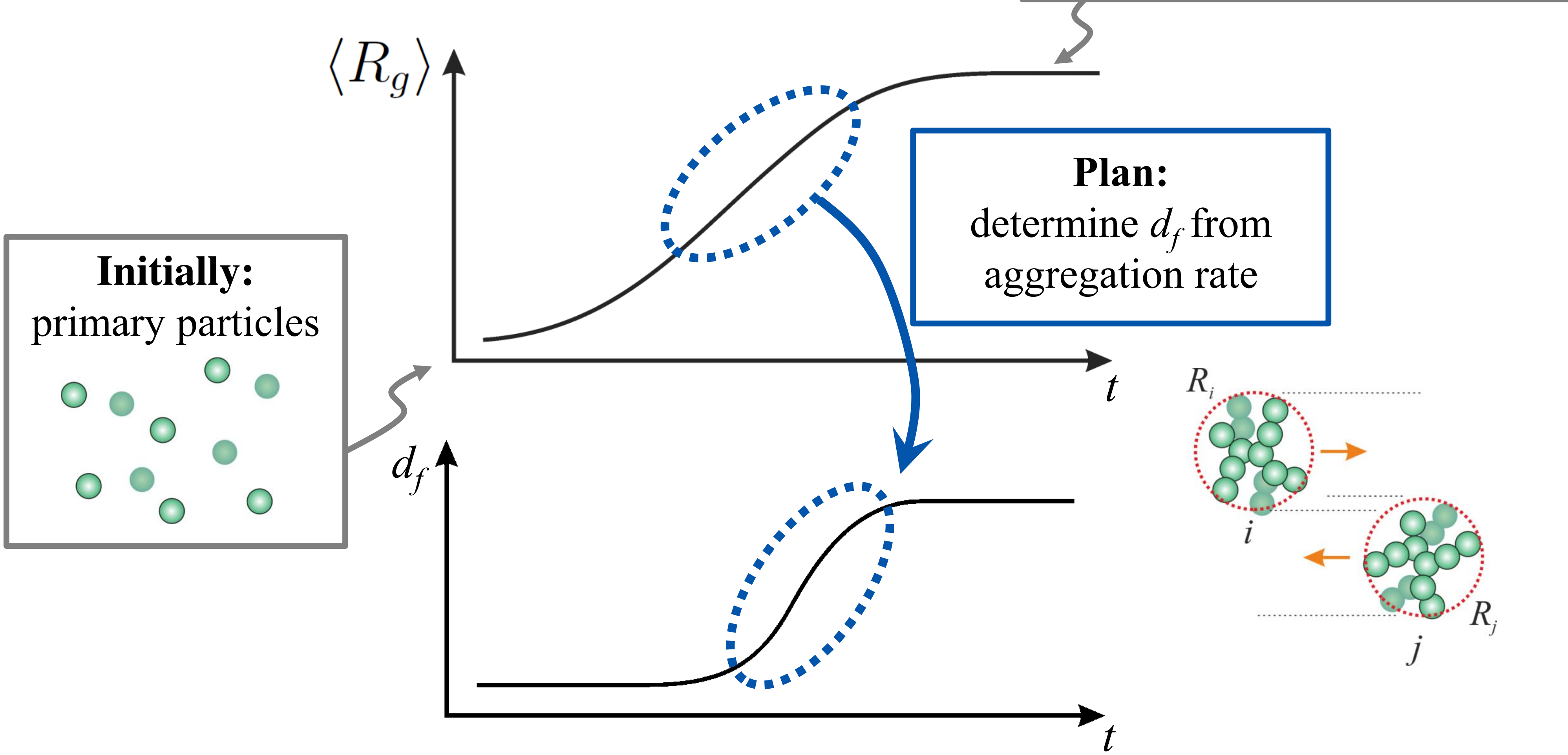
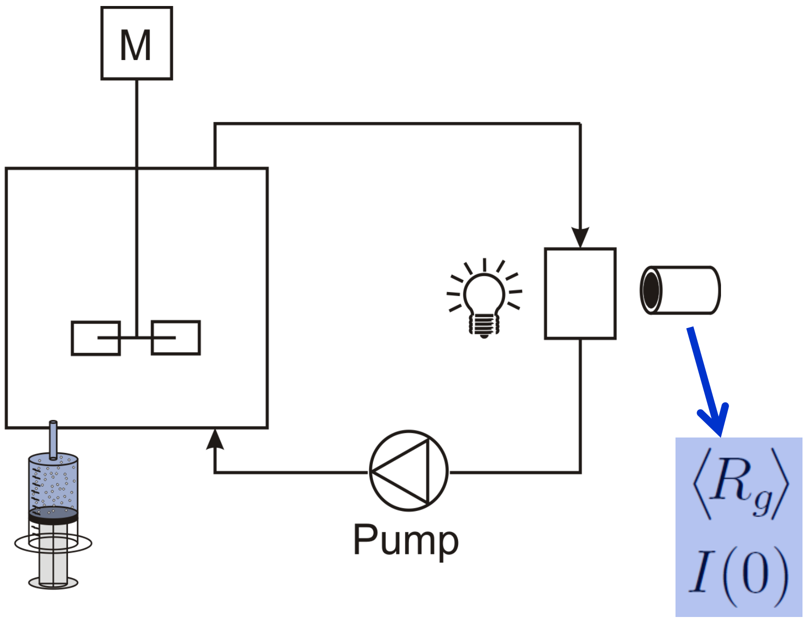
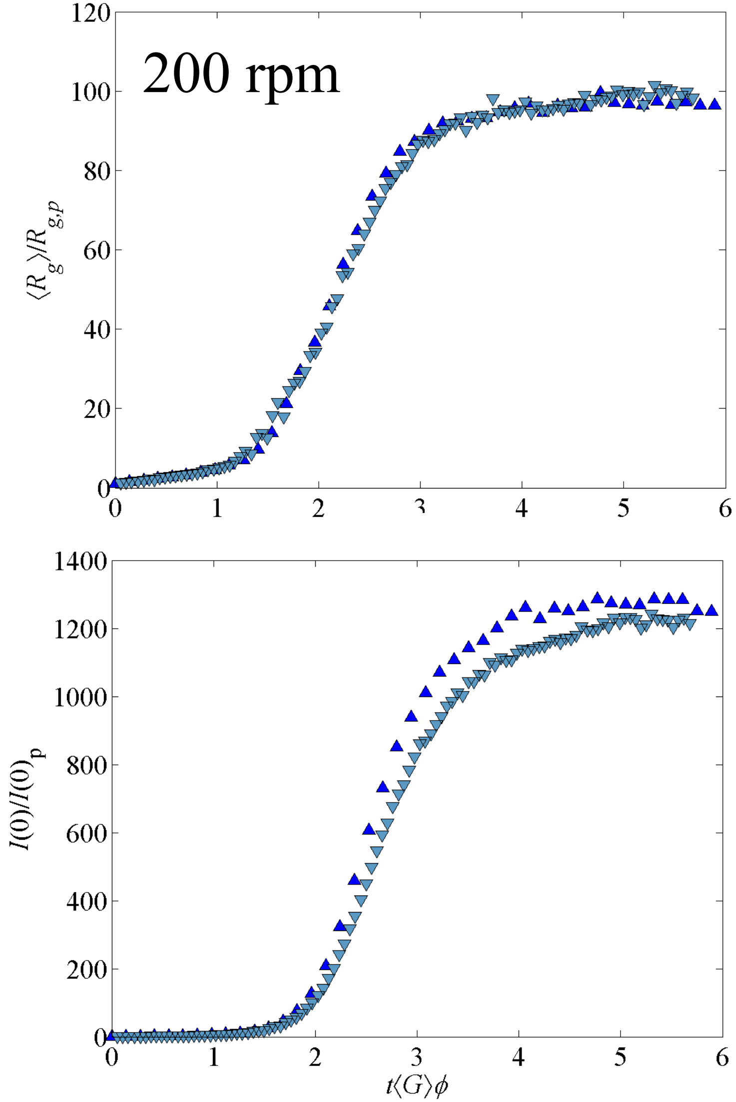




Experimental



- Polystyrene particles
- $d_p = 420$ nm, $\phi = 2 \times 10^{-5}$
- Coagulant: $Al(NO_3)_3$, 0.16 w%
- Fully destabilized particles



Ehrl *et al.*, *Langmuir* (2009)

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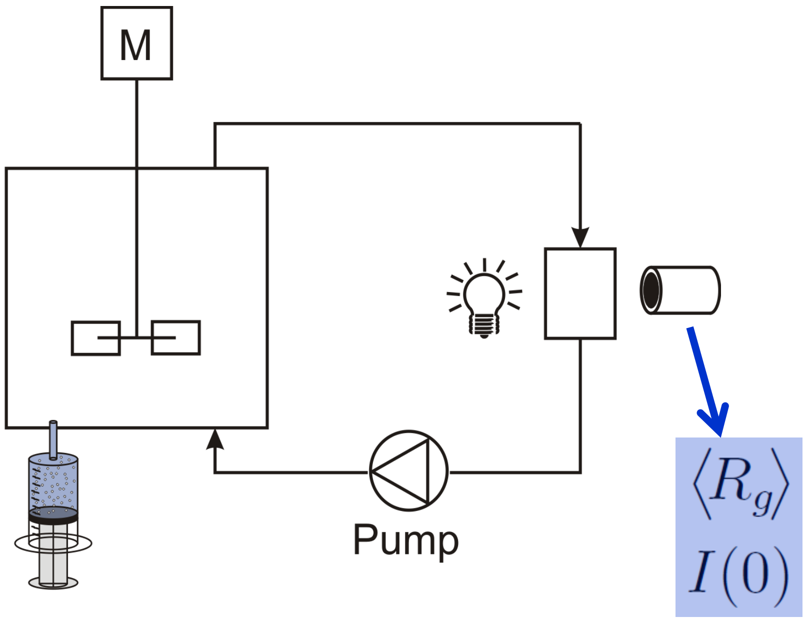

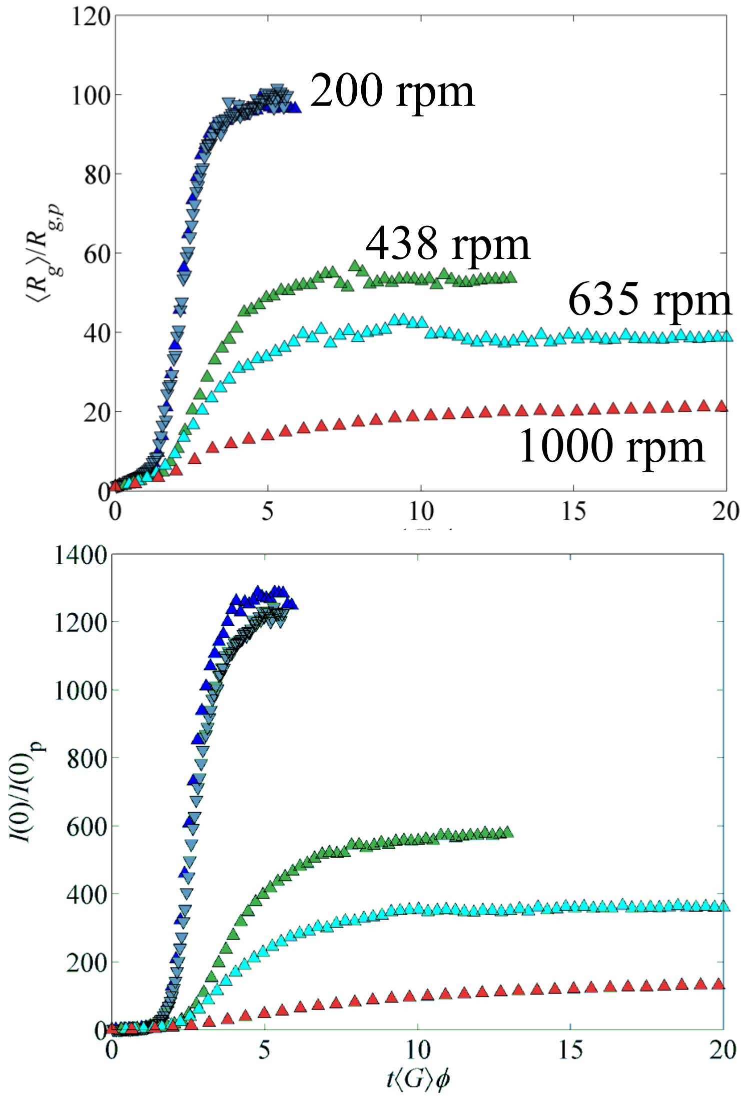

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Population balance model

$$\frac{dN_i}{dt} = \frac{1}{2}\sum_{j=1}^{i-1} K_{A,j,i-j} N_j N_{i-j} - N_i \sum_{j=1}^{\infty} K_{A,i,j} N_j$$

$$- K_{B,i} N_i + \sum_{j=i+1}^{\infty} g_{i,j} K_{B,j} N_j$$

Population balance model

$$d_f(t)$$

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- **Aggregation** ⟶ Saffman&Turner type [1]
- **Breakup** ⟶ Critical stress model [3]
  Binary breakup
- **Evolving d_f** ⟶ Pre-described function

[1] Babler, AIChE J. (2008), [2] Babler et al., Langmuir (2010), [3] Babler et al. J. Fluid Mech. (2008), Babler et al. PRE (2012)

Population balance model

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- **Aggregation** ⟶ Saffman&Turner type [1]
- **Breakup** ⟶ Critical stress model [3]
  Binary breakup
- **Evolving d_f** ⟶ Pre-described function

- Light scattering model [2]

$$\frac{\langle R_g \rangle}{R_{g,p}} = \left(\frac{\sum_{i=1}^{\infty} i^{d_f(2-c)} N_i}{\sum_{i=1}^{\infty} i^{2-c} N_i} \right)^{1/2}$$

$$\frac{I(0)}{I(0)_p} = \frac{\sum_{i=1}^{\infty} i^{2-c} N_i}{\sum_{i=1}^{\infty} i N_i}$$

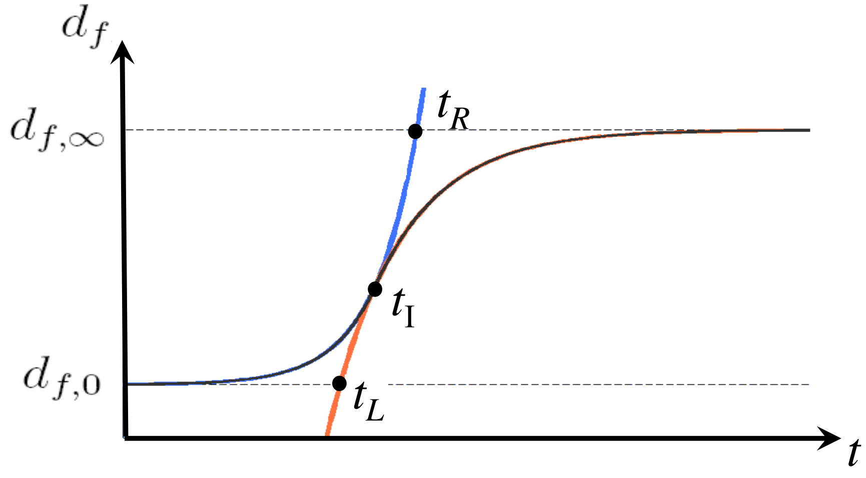
$c =$ correction factor for muliple scattering, important for

- large aggregates
- dense aggregates

[1] Babler, AIChE J. (2008), [2] Babler et al., Langmuir (2010), [3] Babler et al. J. Fluid Mech. (2008), Babler et al. PRE (2012)

Evolving fractal dimension

- Pre-described funtion evolving smoothly between two plateaus



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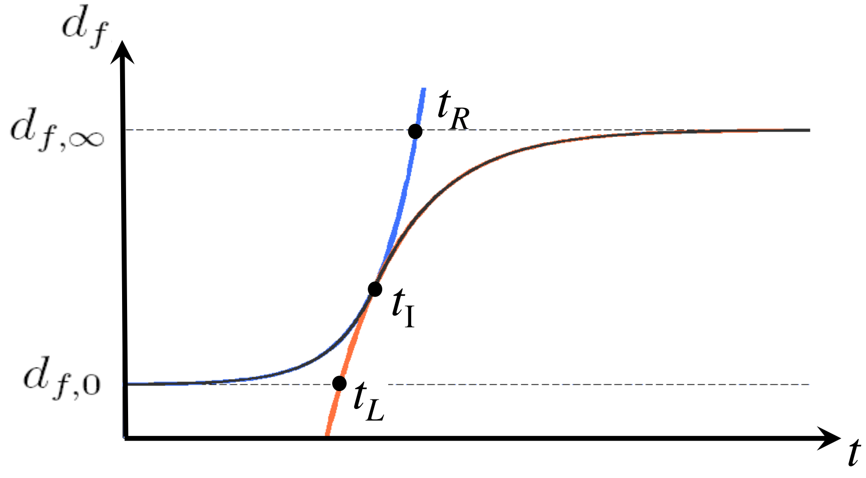
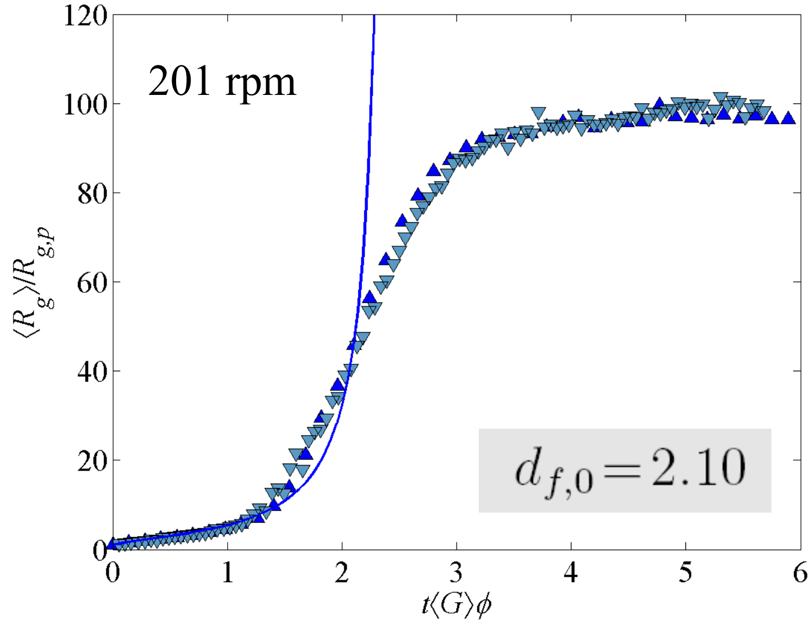
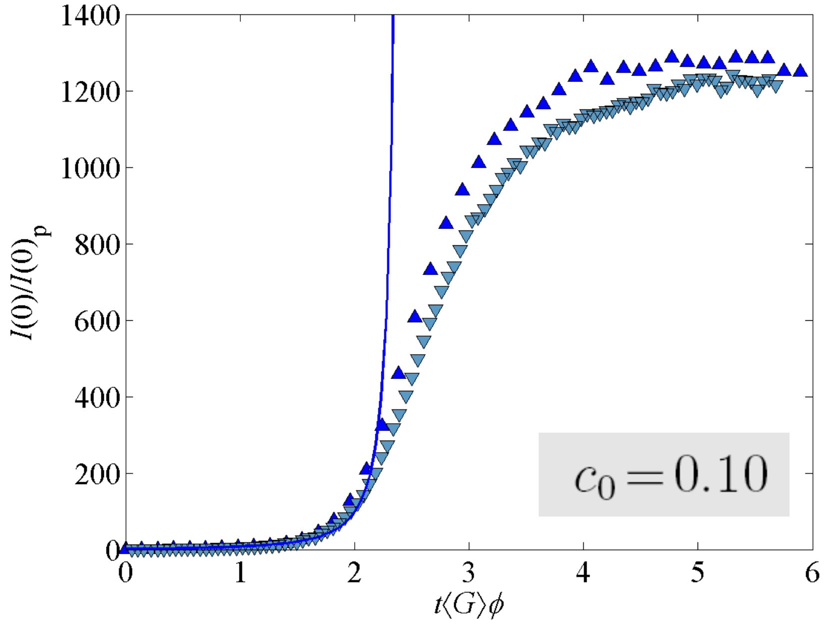


Initial fractal dimension





Evolving fractal dimension

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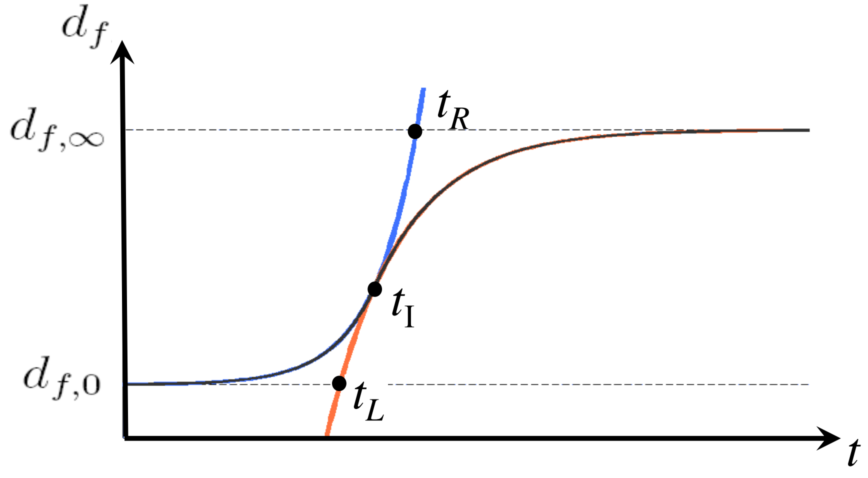
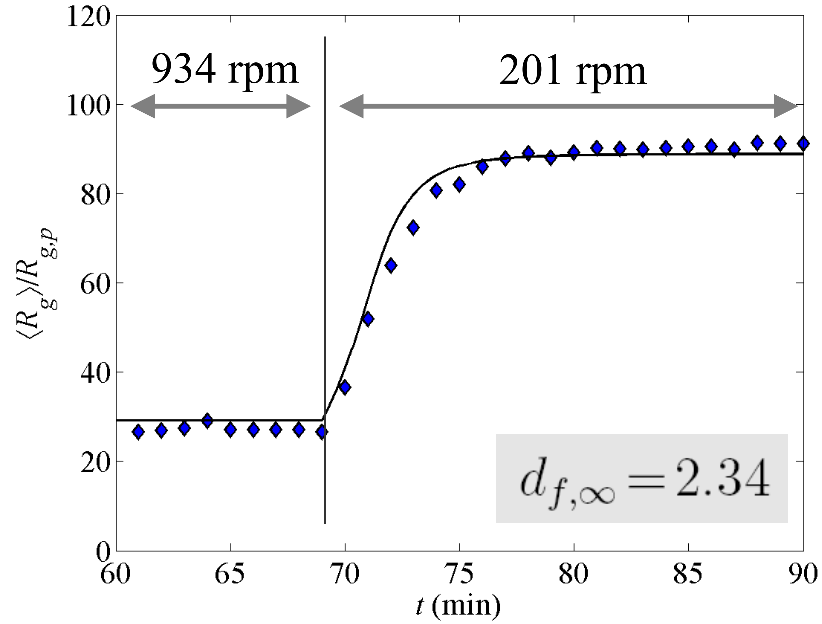
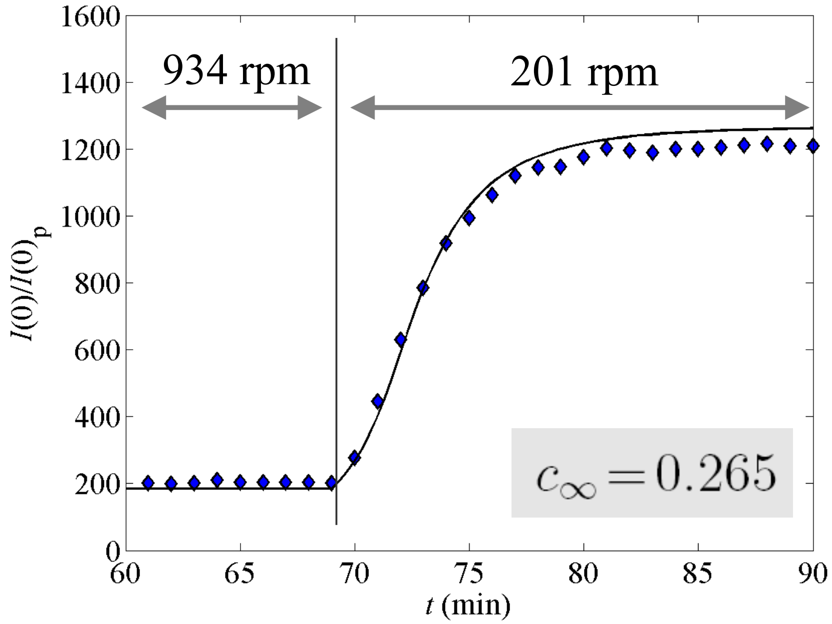
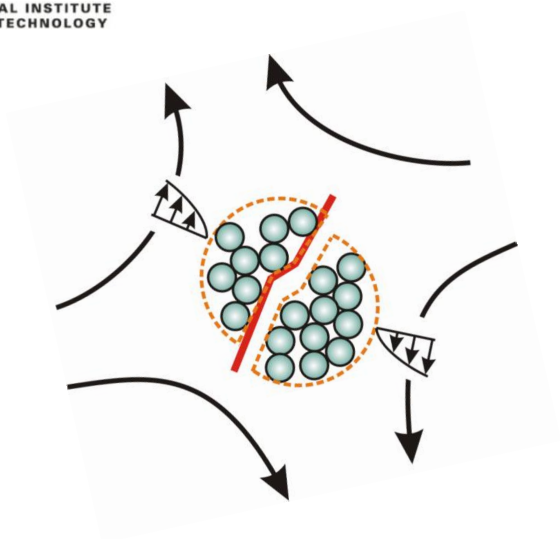


Final fractal dimension



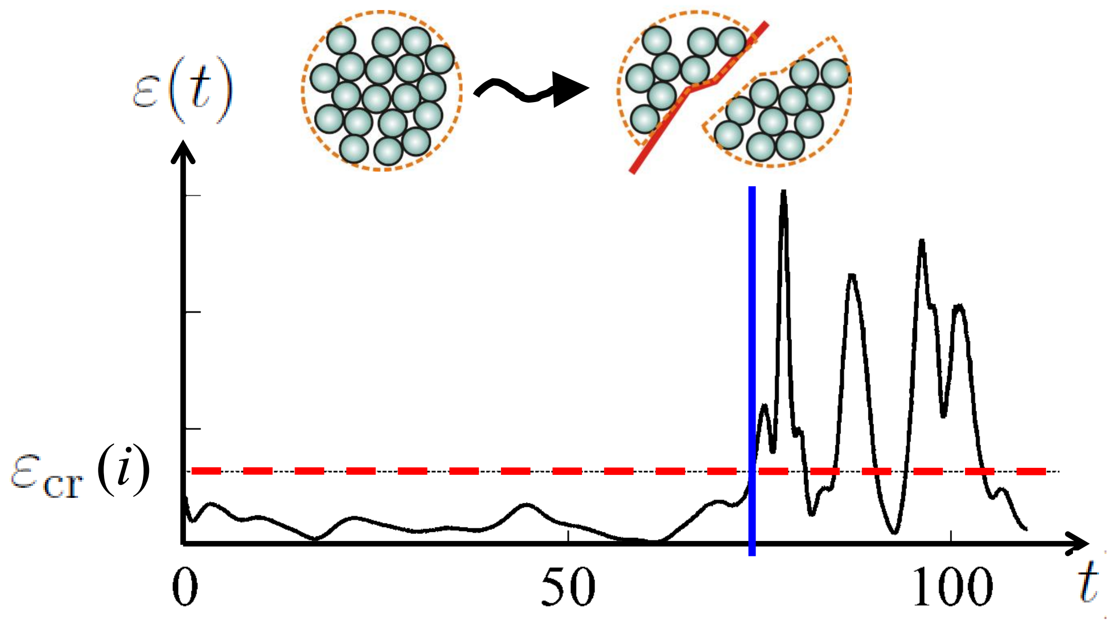


Aggregate breakup in turbulence



- ∃ critical stress $\sigma_{cr} = \sigma_{cr}(i)$
- Instanteneous breakup
- Small, inertialless particles

$$\sigma \sim \mu(\nu/\varepsilon)^{1/2}$$

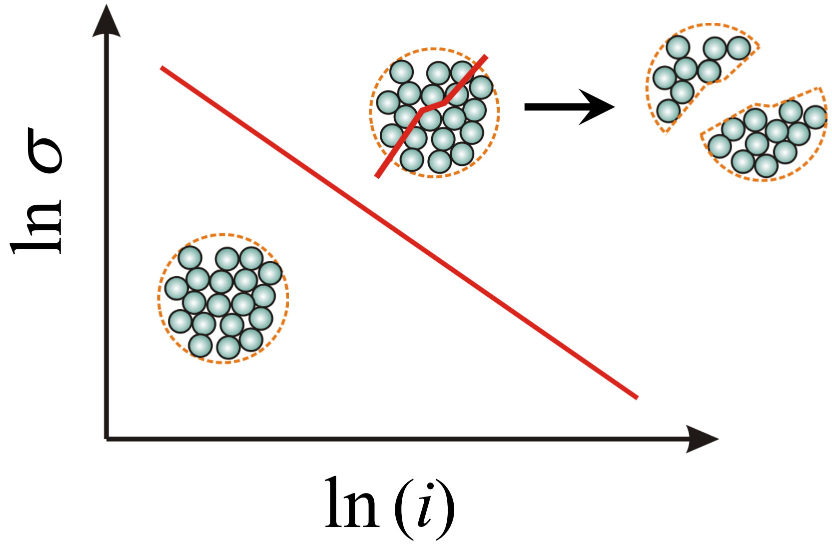


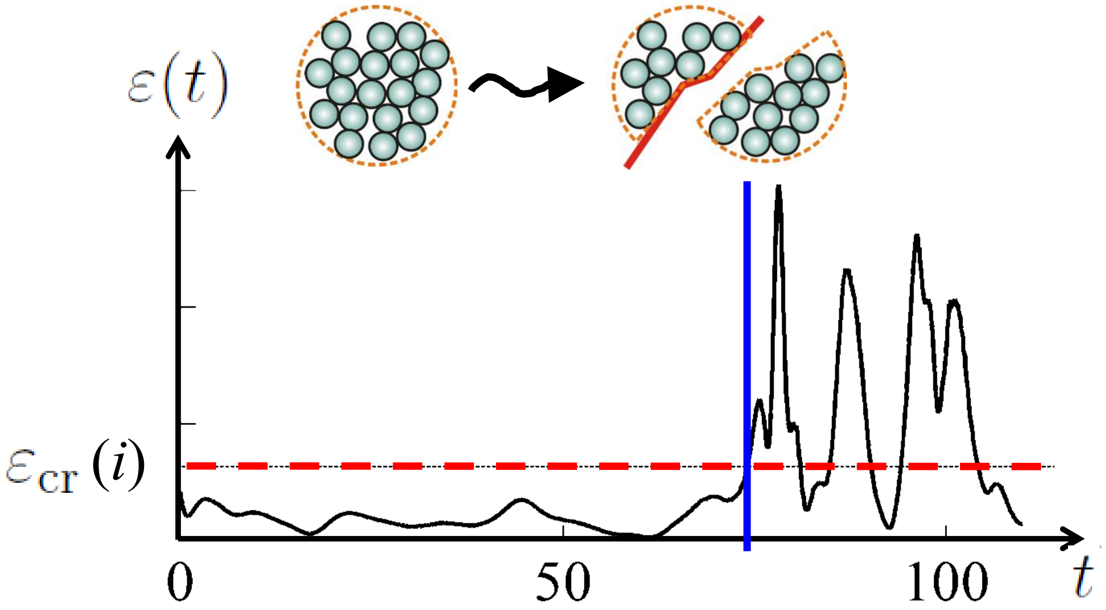
Babler et al. *J. Fluid Mech.* (2008); Babler, Biferale, Lanotte, *PRE* (2012)

Aggregate breakup in turbulence

- Critical stress depends on the aggregate properties, i.e., its "size" (i)
- Power law behavior

$$\sigma_{\mathrm{cr}}(i) \sim i^{-m/2}$$



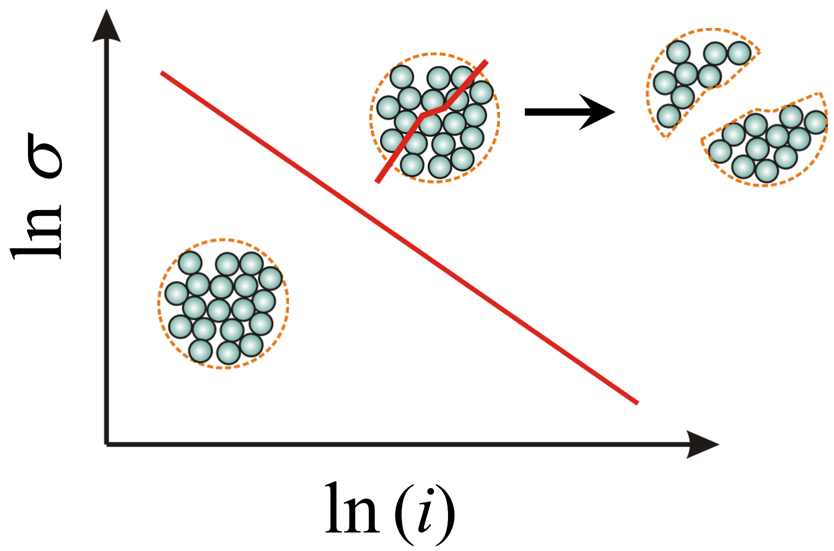


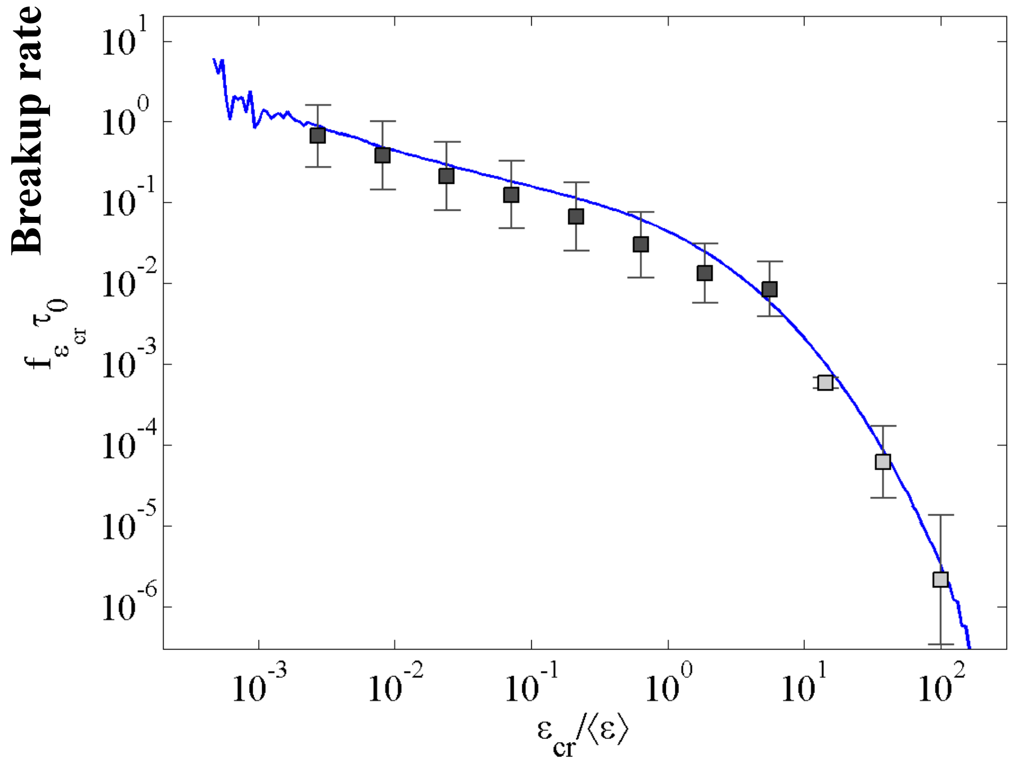
Babler et al. *J. Fluid Mech.* (2008); Babler, Biferale, Lanotte, *PRE* (2012)

Aggregate breakup in turbulence

- Critical stress depends on the aggregate properties, i.e., its "size" (i)
- Power law behavior

$$\sigma_{cr}(i) \sim i^{-m/2}$$





Babler et al. *J. Fluid Mech.* (2008); Babler, Biferale, Lanotte, *PRE* (2012)

Outline

- Introduction
- Structure of aggregates: aggregate fractal dimension
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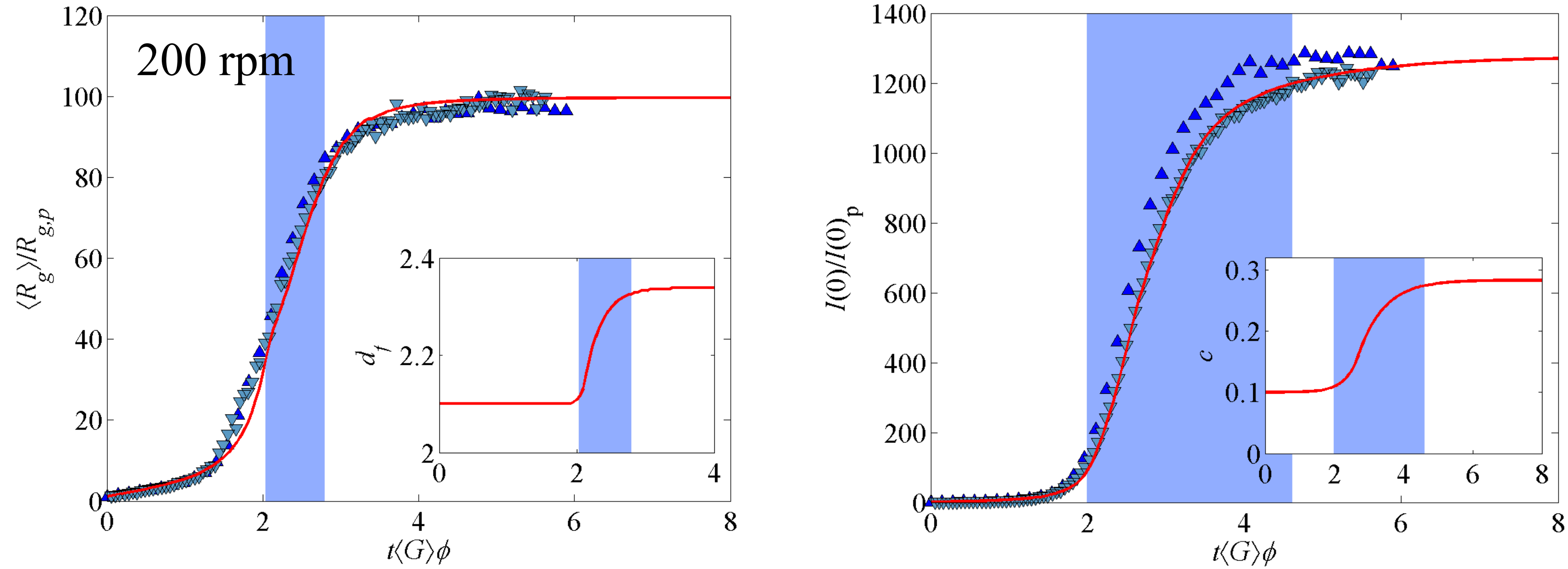
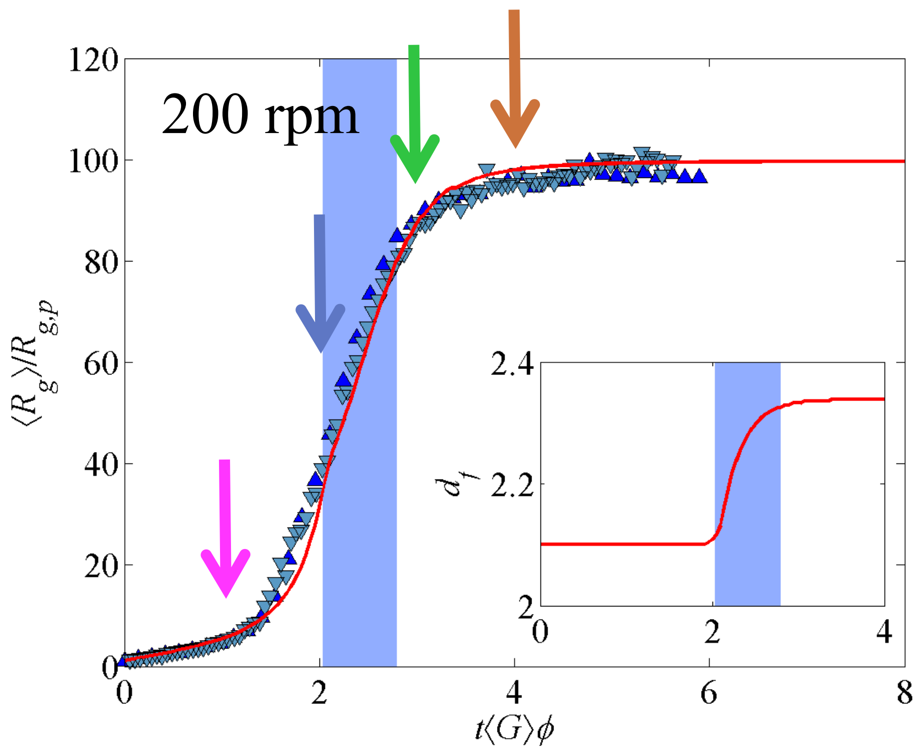
- Breakup model
- **Results**
- Conclusions

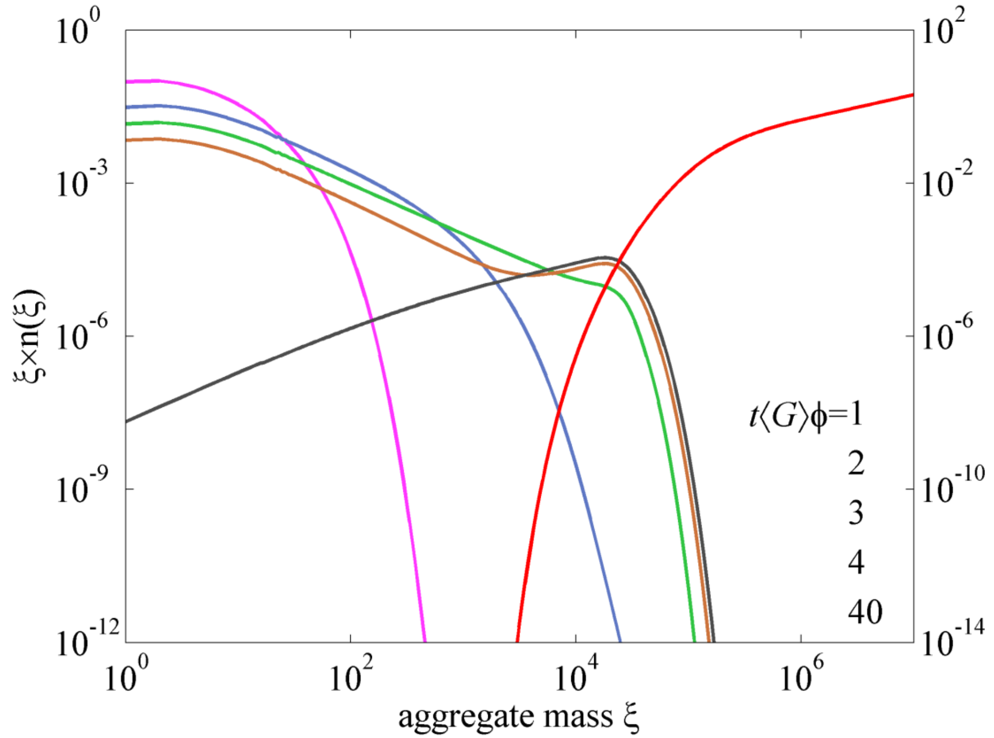
Evolution of fractal dimension



Fitting $d_f(t)$ and $c(t)$ to the evolution of $\langle R_g \rangle$ and $I(0)$

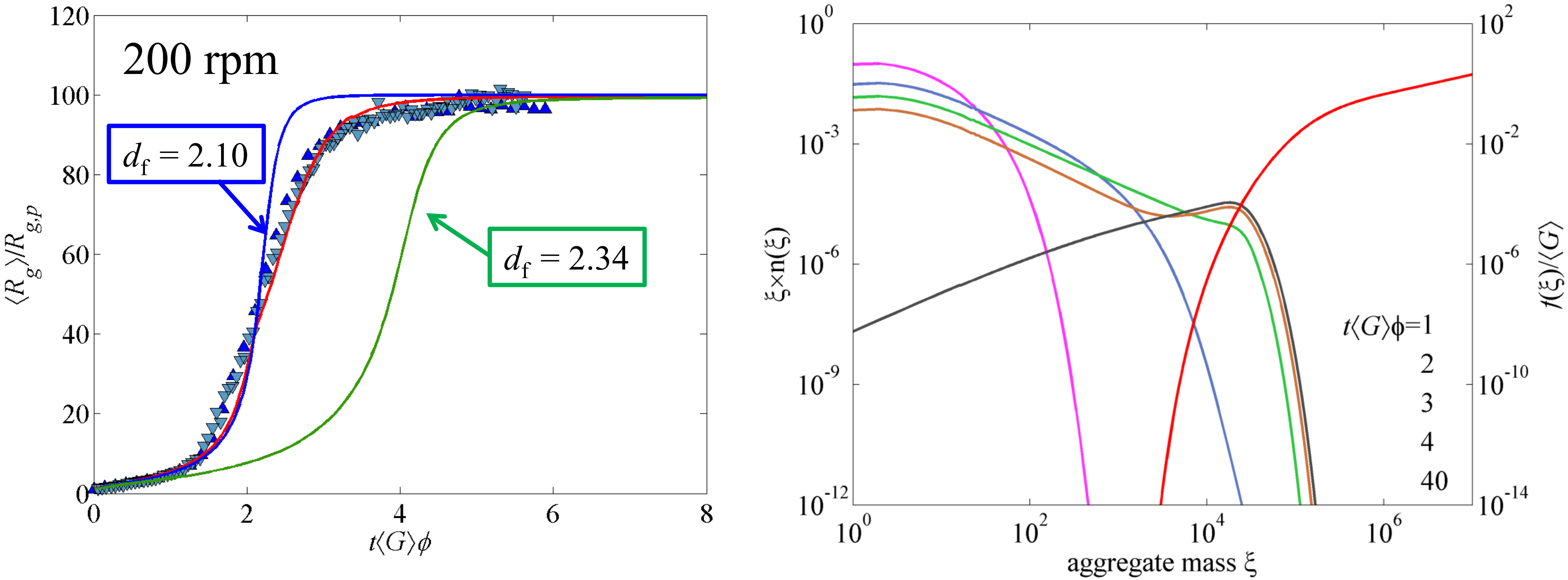
Aggregate size distribution





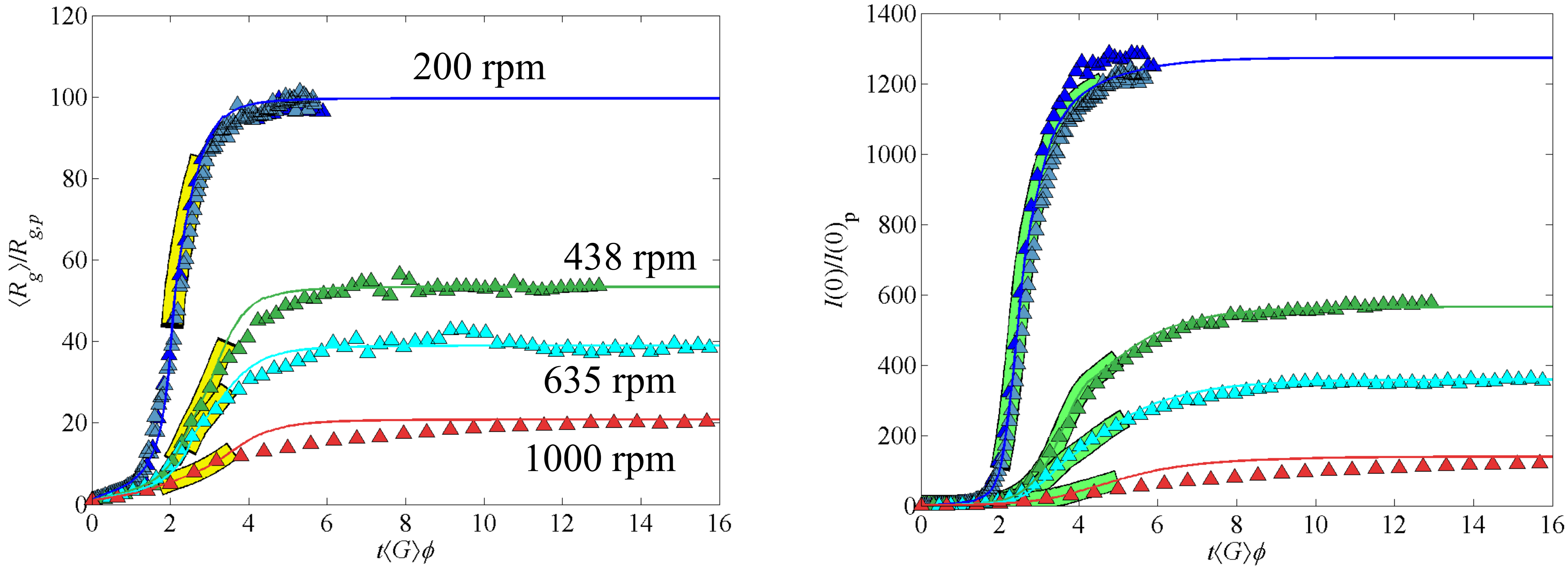
Fitting $d_f(t)$ and $c(t)$ to the evolution of $\langle R_g \rangle$ and $I(0)$

Constant fractal dimension



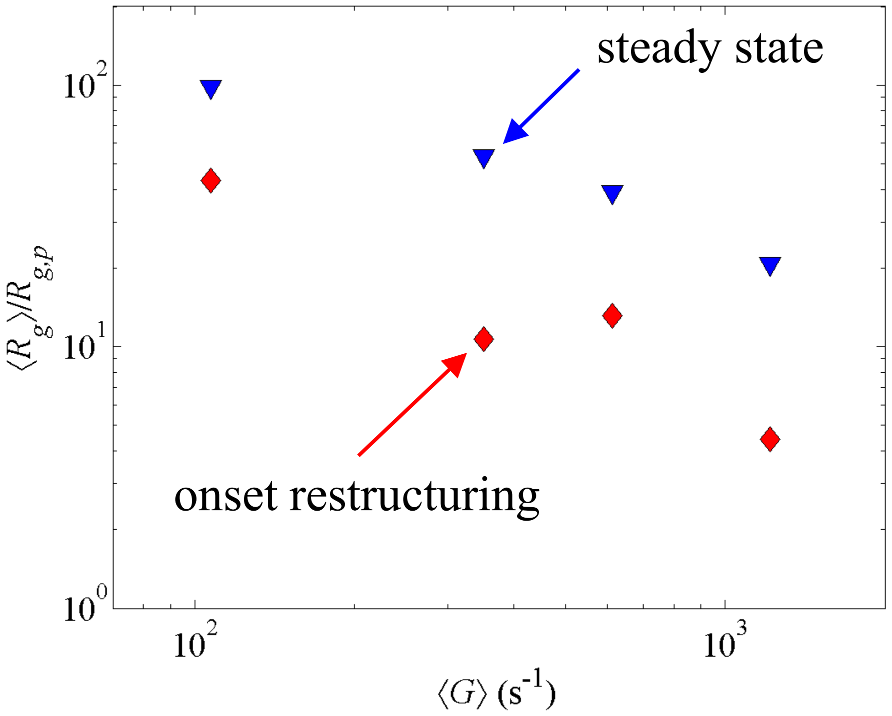
Fitting $d_f(t)$ and $c(t)$ to the evolution of $\langle R_g \rangle$ and $I(0)$

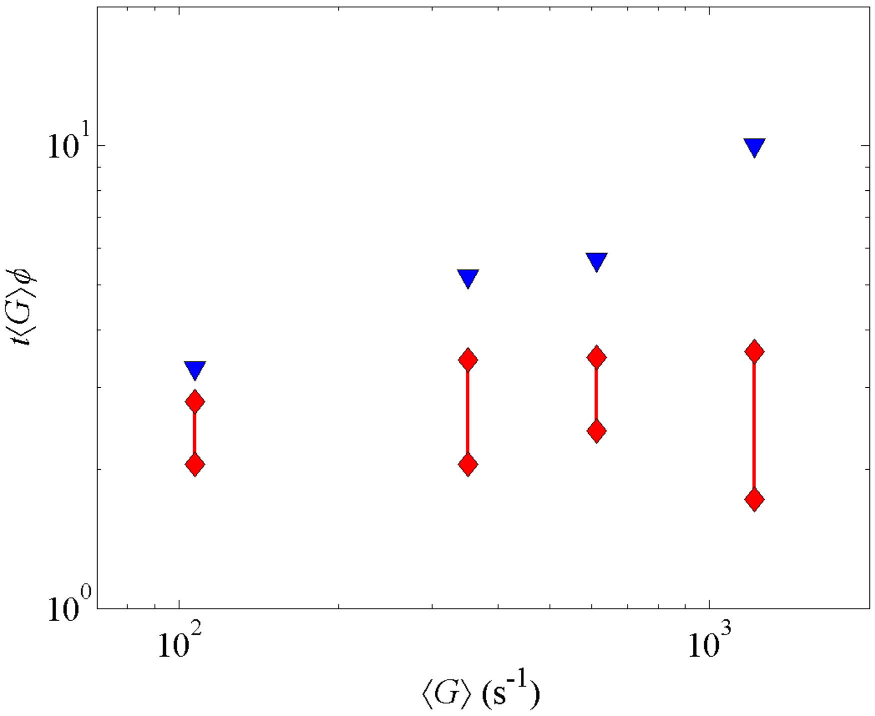
Various stirring speeds



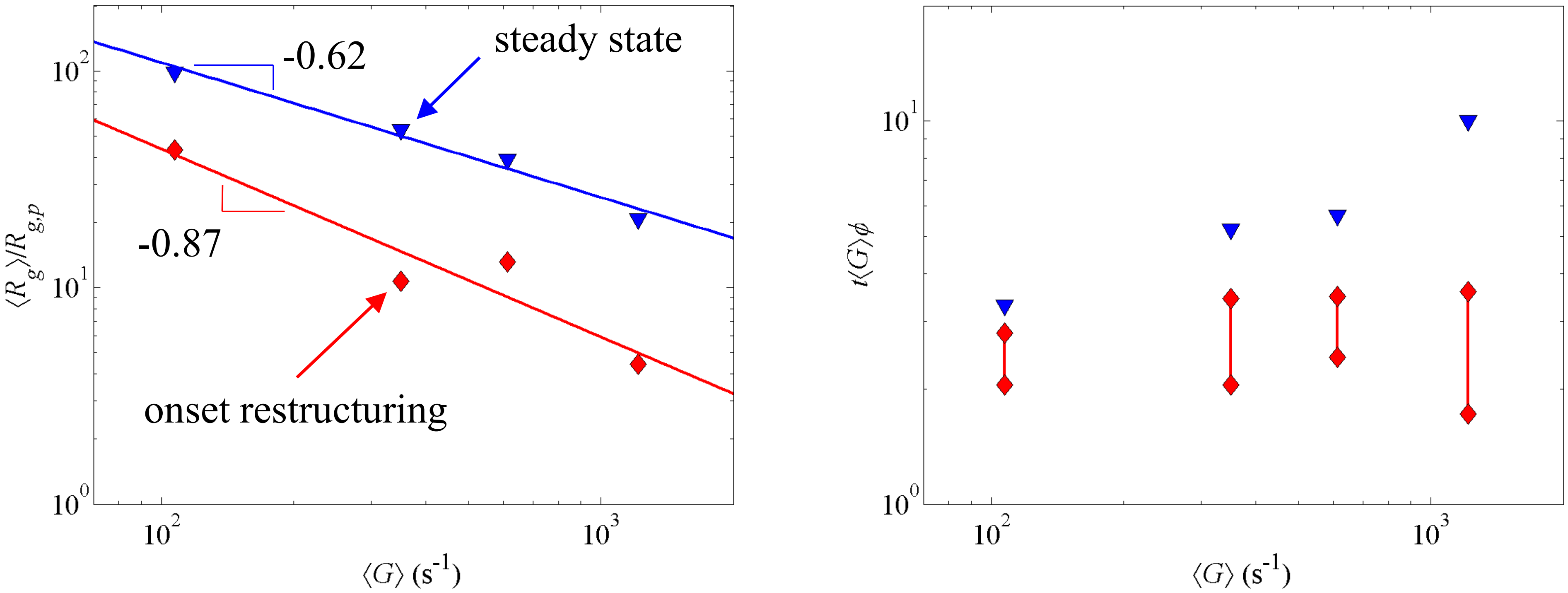
Fitting $d_f(t)$ and $c(t)$ to the evolution of $\langle R_g \rangle$ and $I(0)$

Onset and duration of restructuring



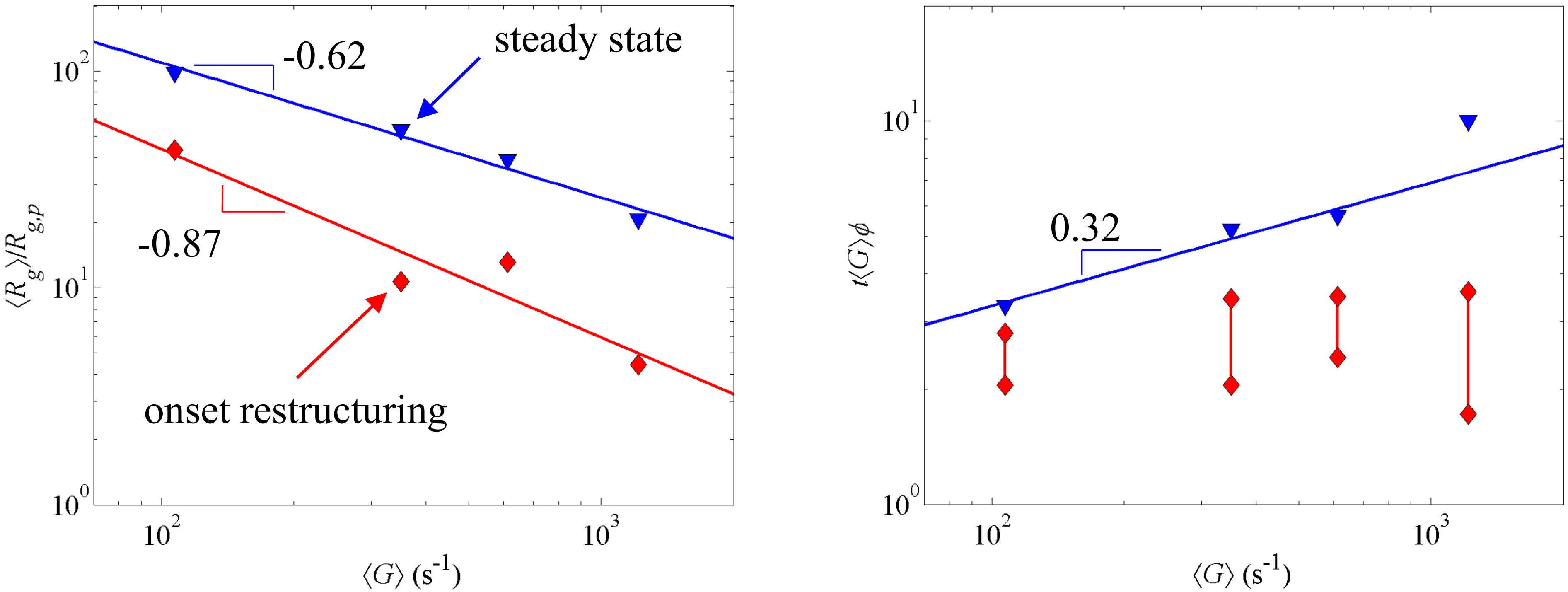


Onset and duration of restructuring



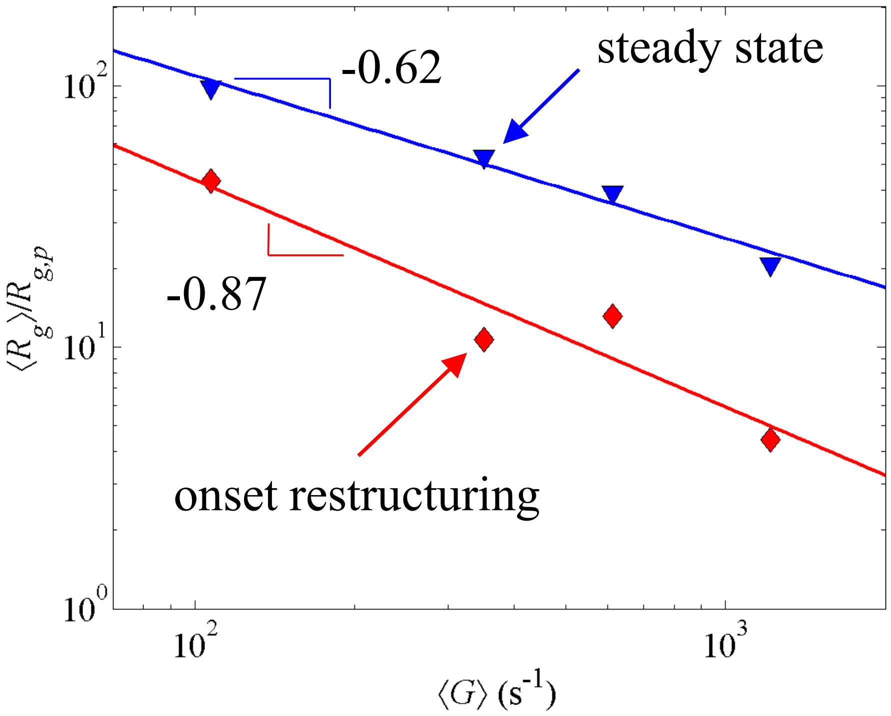
- The onset of restucturing is more sensitive to the shear rate G

Onset and duration of restructuring



- The onset of restucturing is more sensitive to the shear rate G
- The duration of restructuring scales with the shear rate G

Onset and duration of restructuring



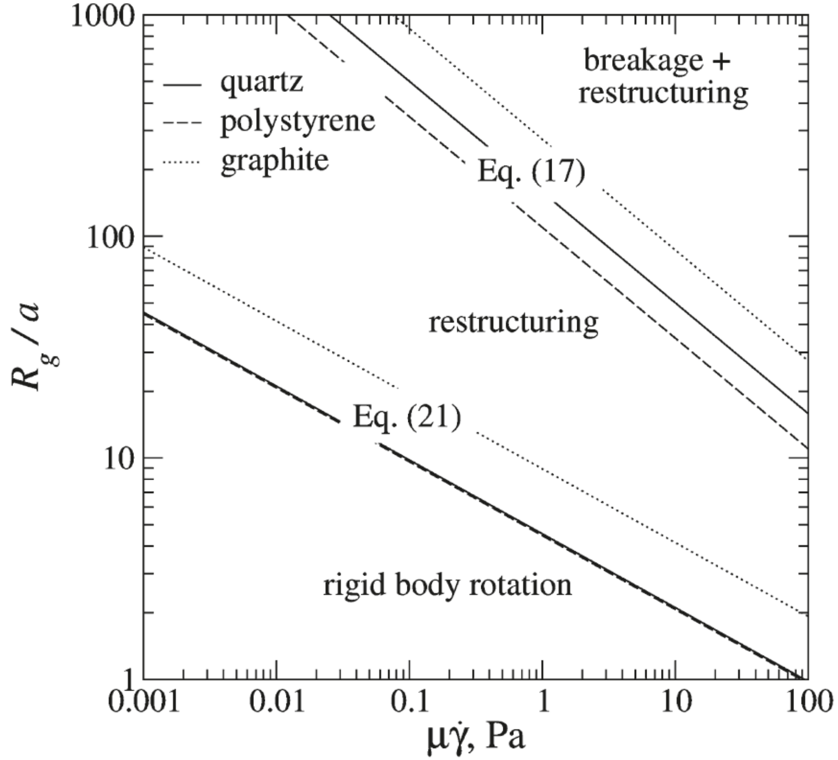


Figure 12. Regime map for restructuring/breakage for fully destabilized suspensions of different materials; $a = 0.5\ \mu$m. The physical data for the considered materials (E, ν, σ) were taken from Dominik and Tielens.[21]

Vanni and Gastaldi, *Langmuir* (2011)

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Conclusions

- Restructuring, in terms of the evolution of the fractal dimension, has been explored by fitting a PBE model to a set of experimental data.
- Restructuring sets in as the aggregates reach a certain size, and it is finished before they reach the steady state size.
- The aggregate size for the onset of restructuring depends stronger than predicted by considering only stress induced restructuring. This hints to collision induced restructuring.
- Restructuring is relatively fast and its duration scales approximately with the shear rate.
- Macromixing and variations of d_f among the aggregates might become relevant at high stirring speeds.

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