Modeling of nanoparticles precipitation in a Confined Impinging Jets Reactor by means of Computational Fluid Dynamics

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Outline

Motivation

- Objective
- Production of polymeric nanoparticles via solvent displacement
- Influence of mixing on the precipitation process
- Static mixers: the Confined Impinging Jets Reactor

Background theory

- Precipitation model
- Flow field modeling: RANS and LES
- mPIV flow field measurements

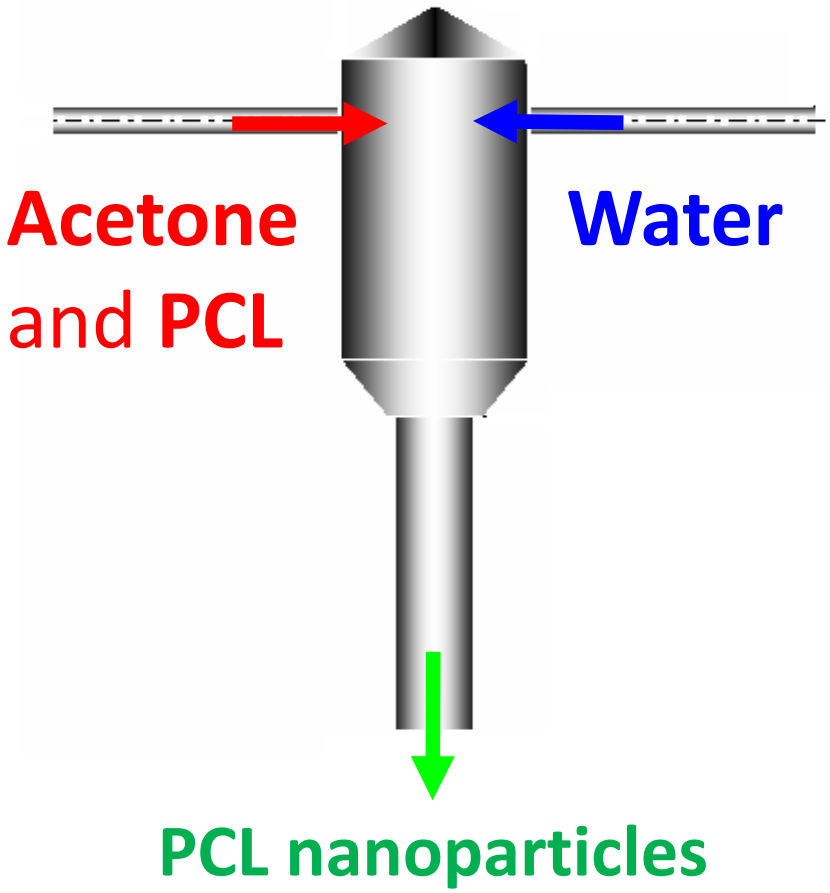
Results

- Modeling of a test reaction: Barium sulfate precipitation
- Flow field in the CIJR: μPIV experiments vs Large Eddy Simulations

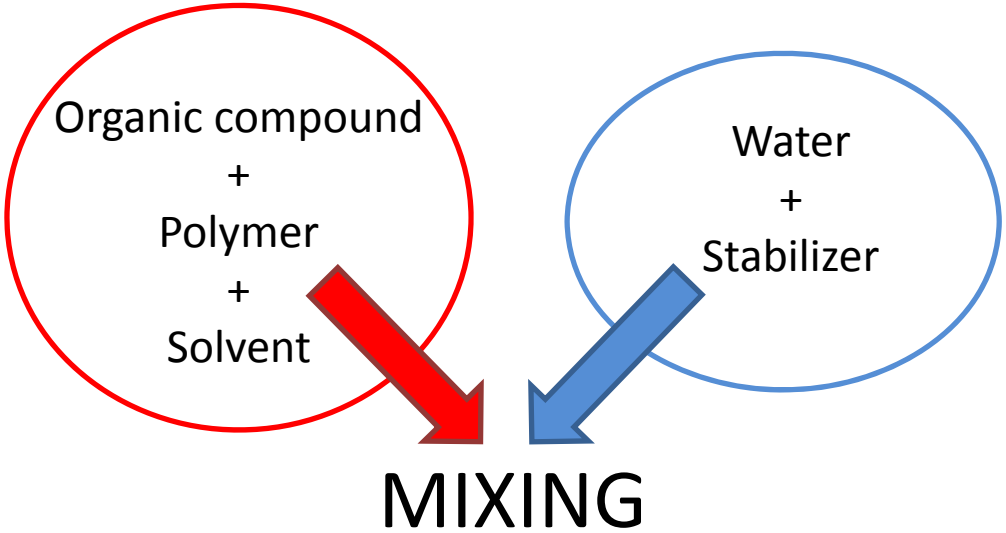
Conclusions and next steps

Objective

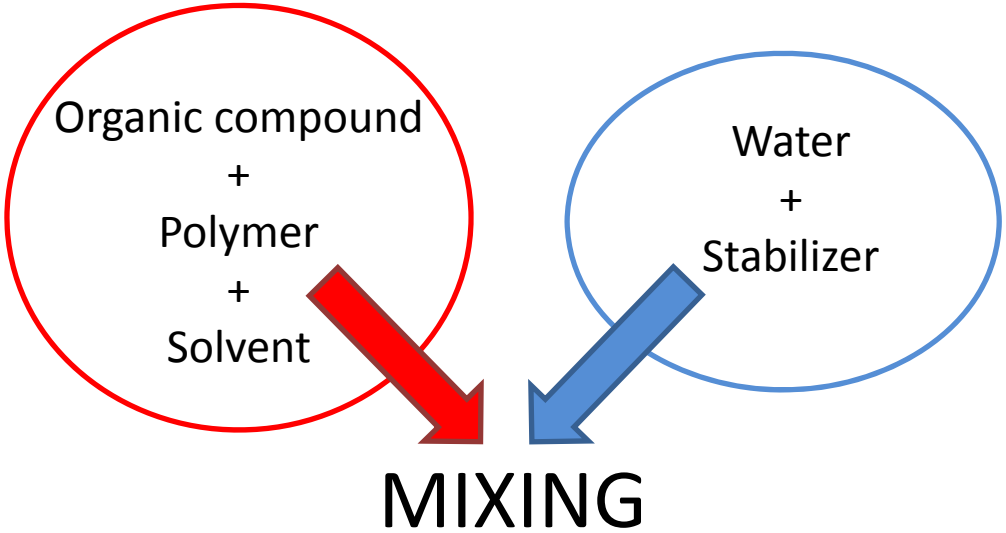
- CFD Modeling of polycaprolactone (PCL) nanoparticles precipitation via solvent displacement in a Confined Impinging Jets Reactor (CIJR)



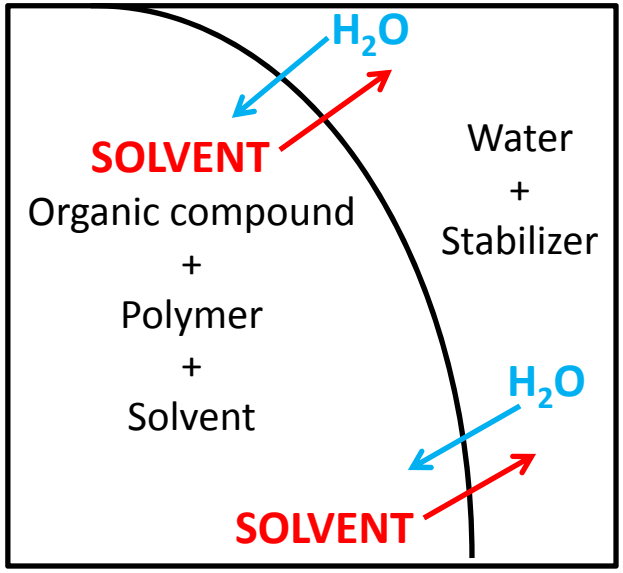
Solvent displacement



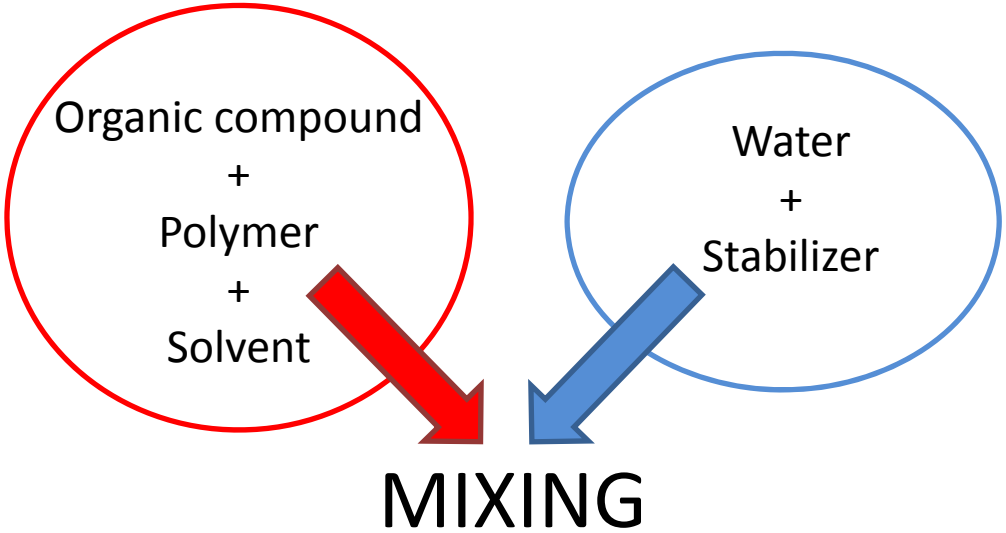
Solvent displacement

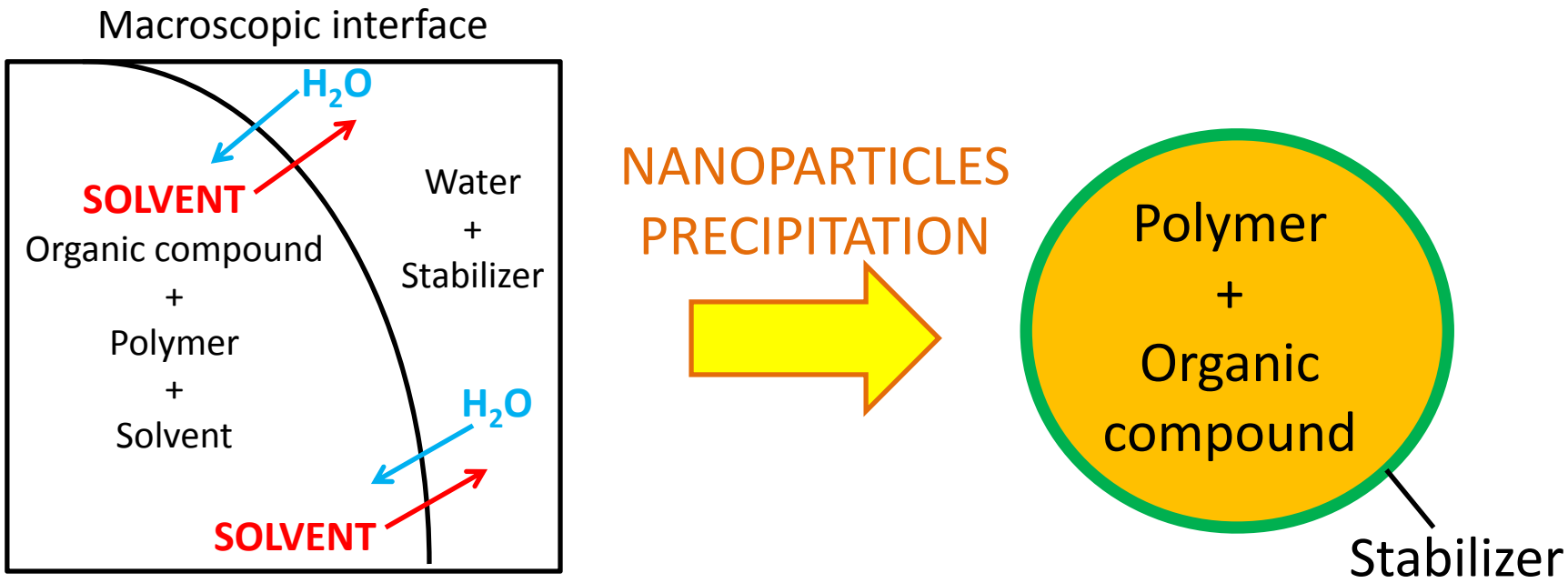


Macroscopic interface



Solvent displacement





Particle Size Distribution

- Operating conditions influence PSD
  - Initial reactants concentration
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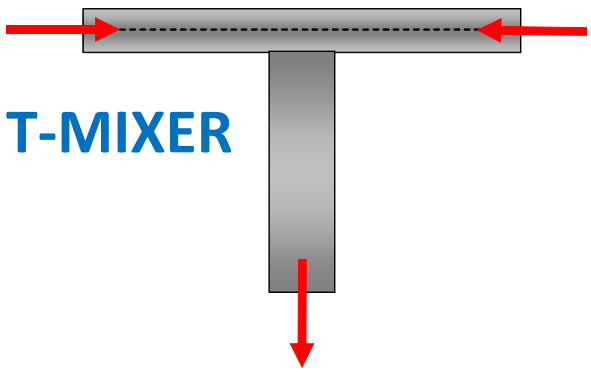
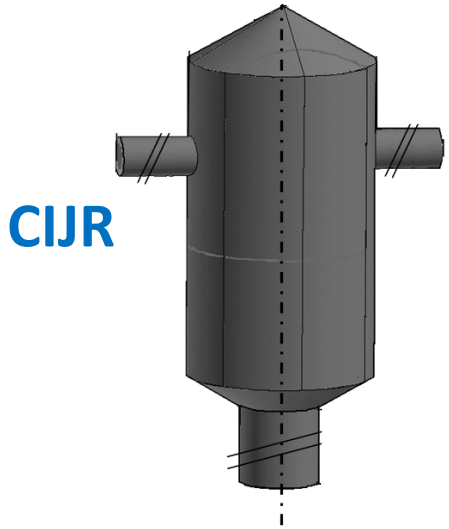
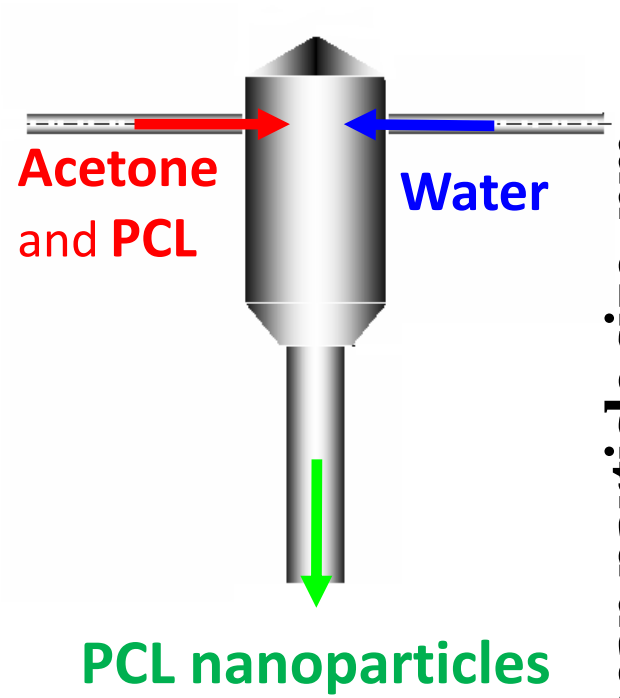
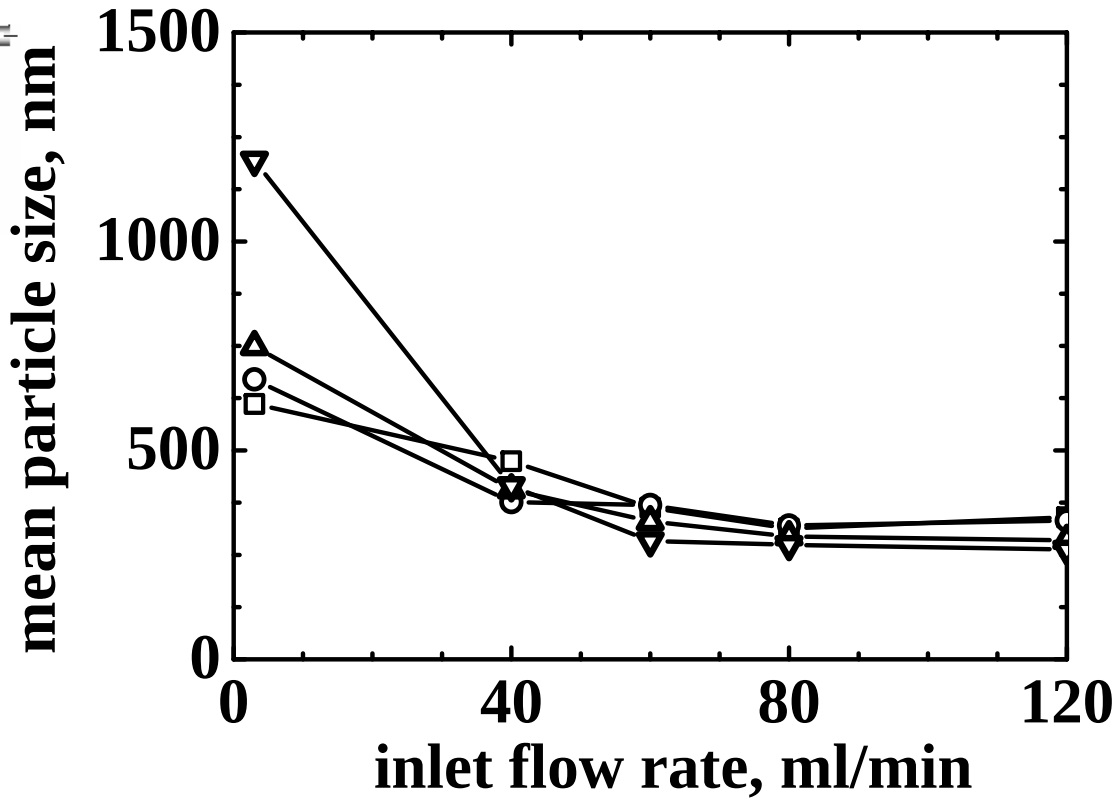




Effect of mixing on PSD: experiments





M_w = 14000, C_{PCL}^0= 10 mg/ml; W/A = 1 (□), W/A = 2 (○), W/A = 3 (△), W/A = 4 (▽).

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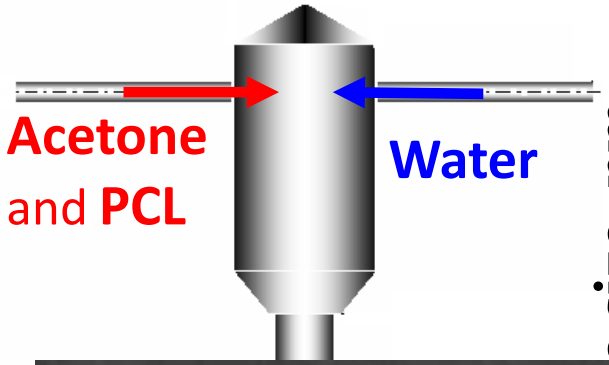
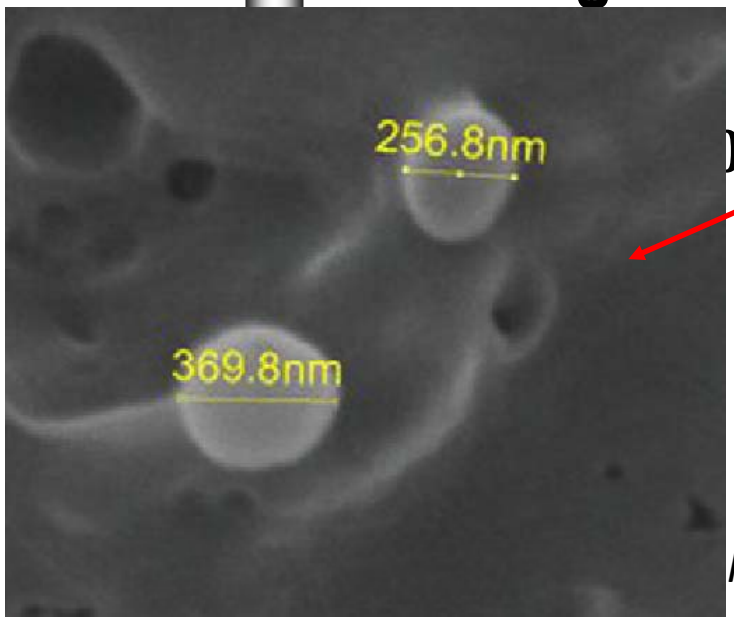
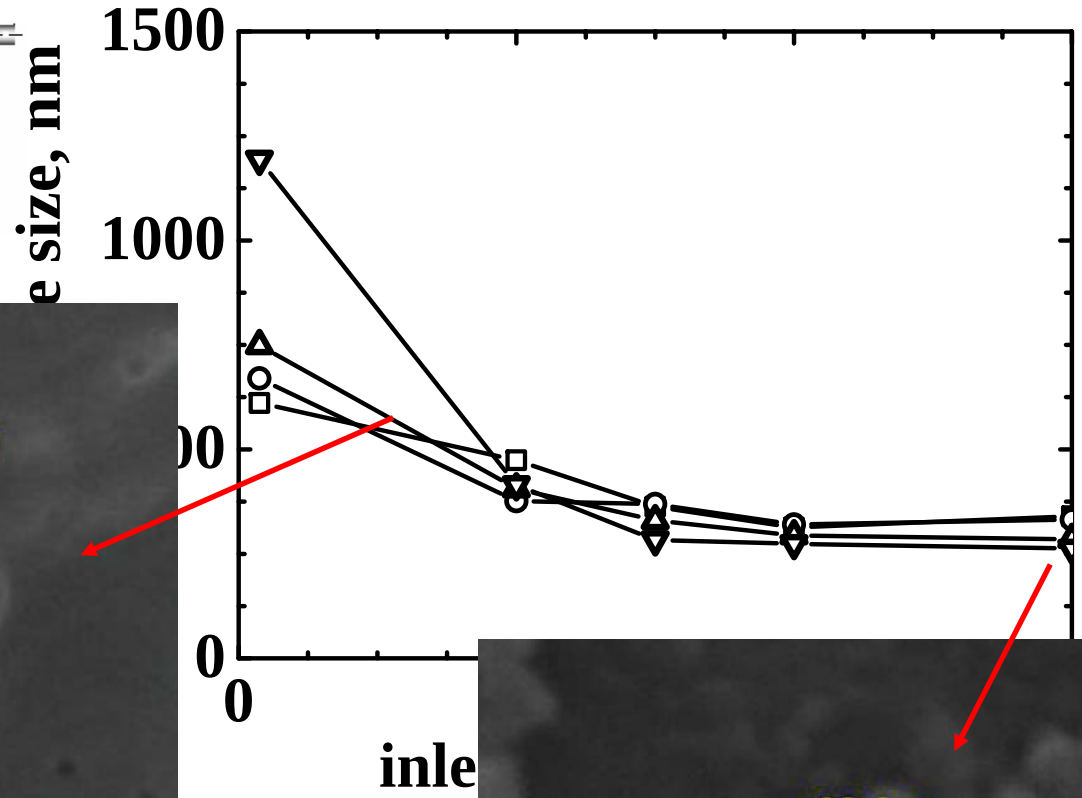
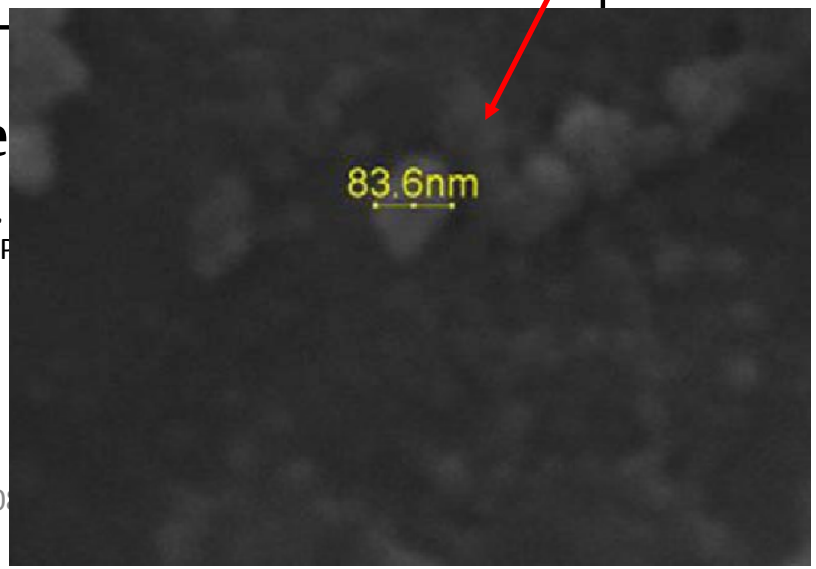


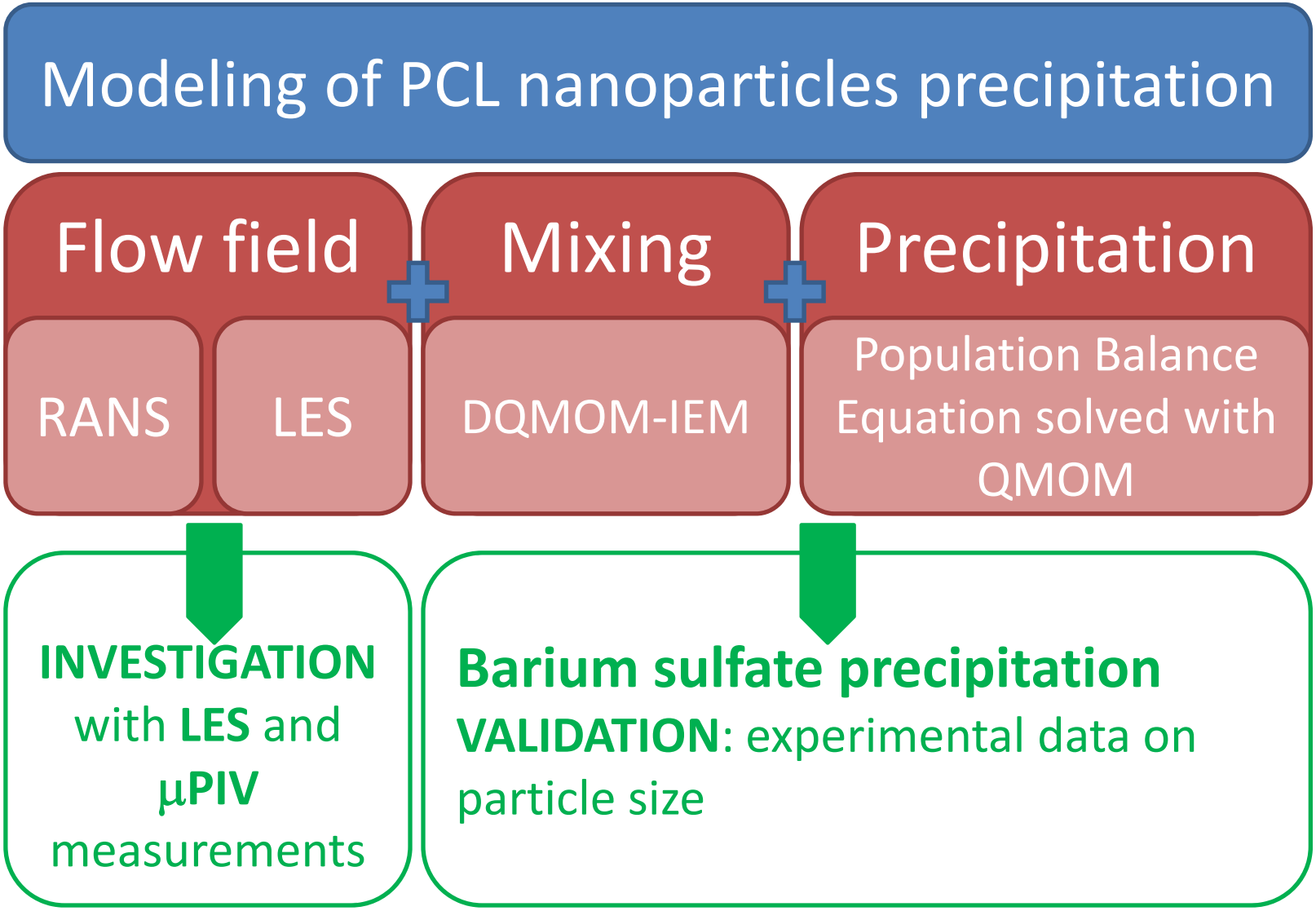




M_w = 14000, C_P
= 2 (○), W/A =



Study outline

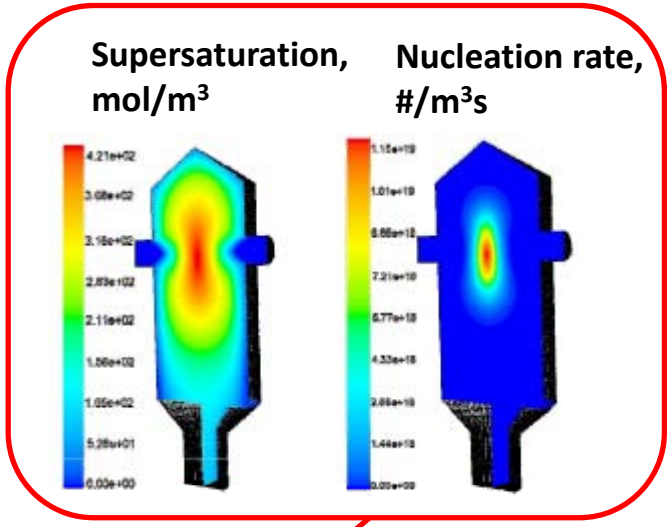


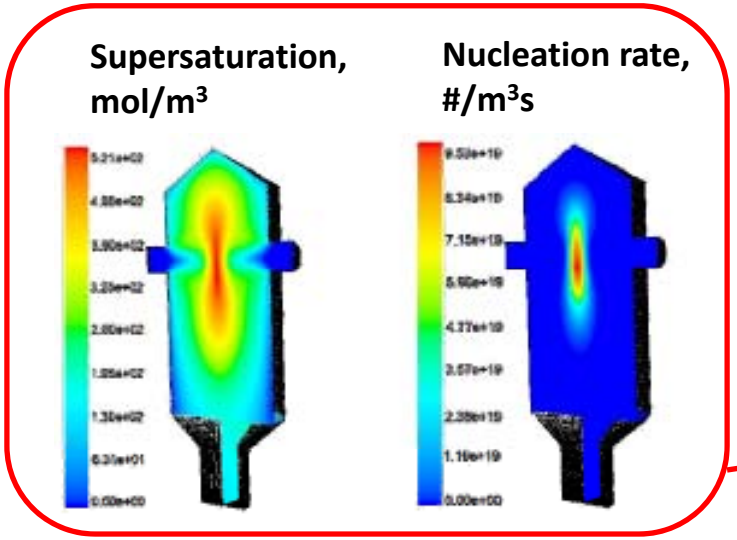
Precipitation model: effect of mixing

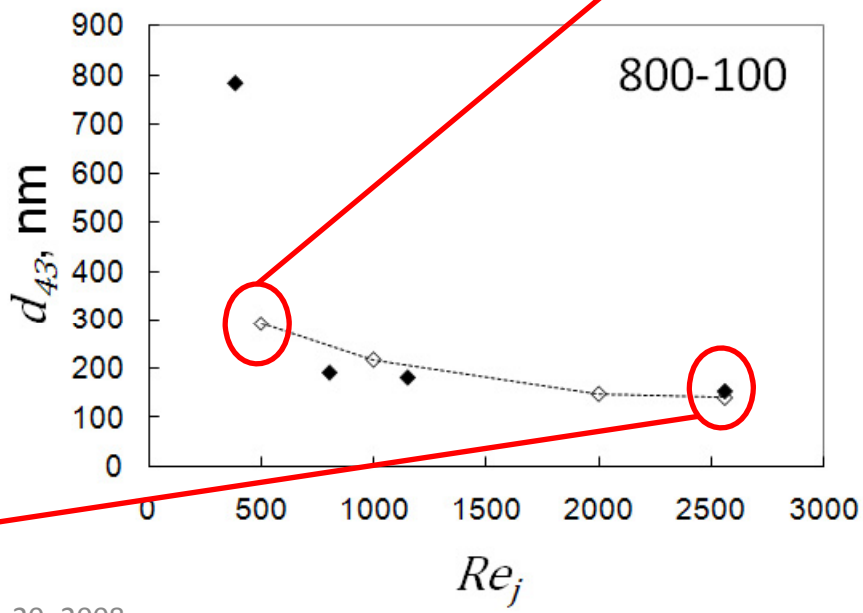
- Nucleation and growth rate modeled from classical precipitation theory (Schwarzer and Peukert, 2005)
- Supersaturation is produced by the instantaneous reaction

$$BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4(\downarrow) + 2\ NaCl$$

- Mixing influences the reaction and therefore the supersaturation build-up



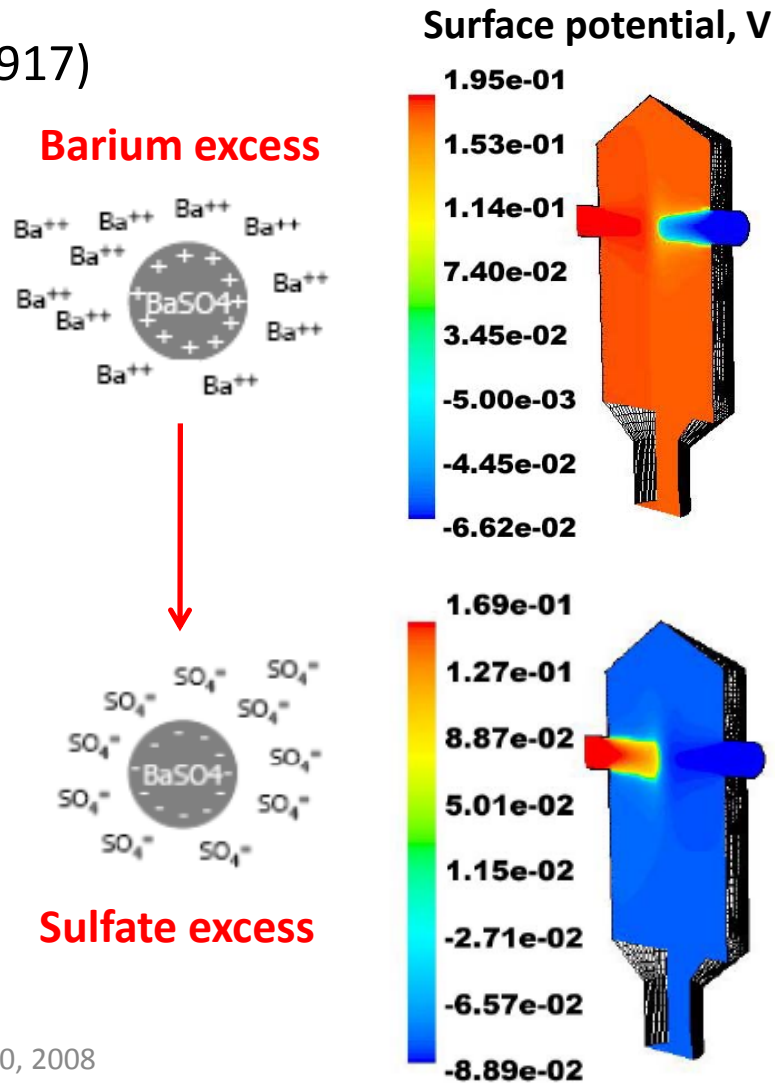




Precipitation model: aggregation

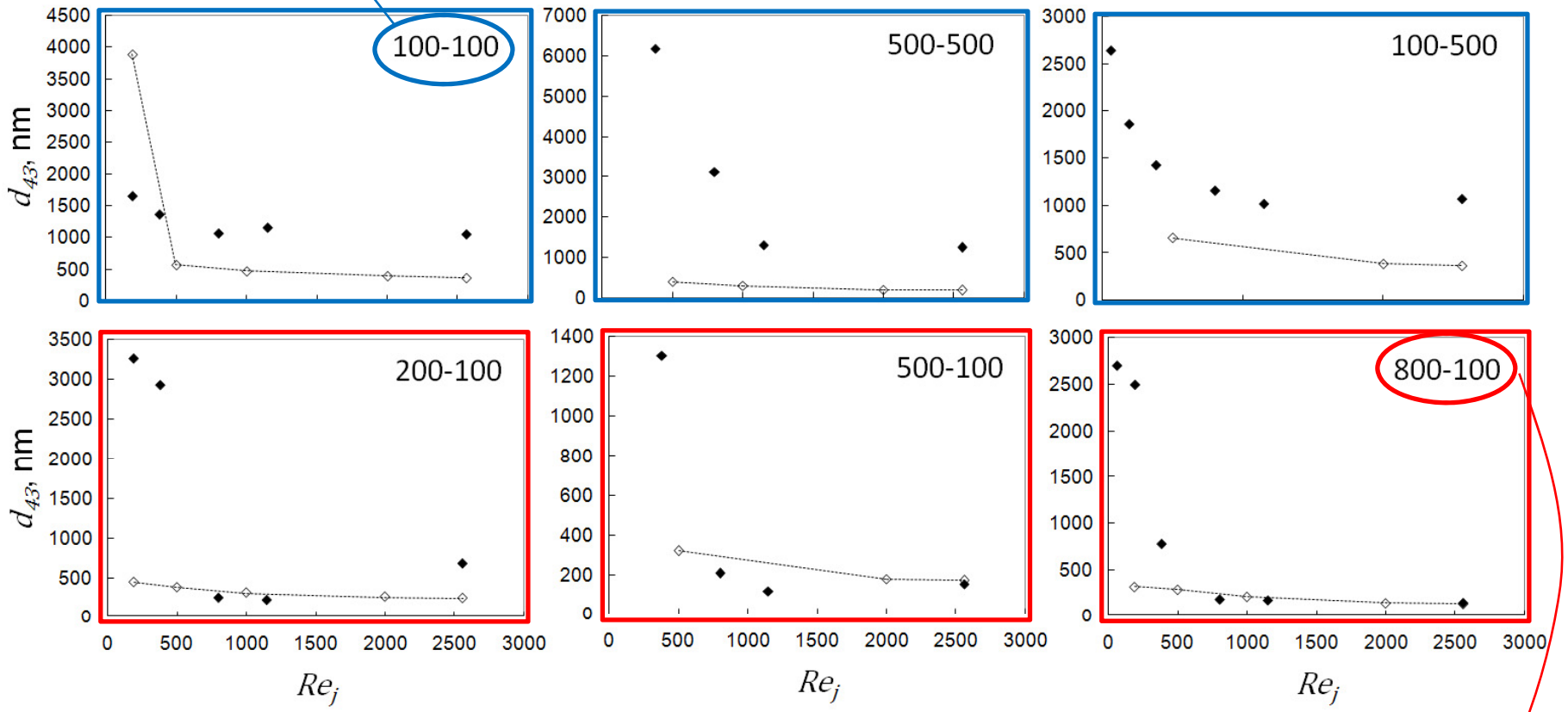
- A transport mechanism is responsible for bringing particles into close proximity
- Two asymptotic limits (Smoluchowski, 1917)
  - –Brownian motions
  - –Shear induced collisions
- Collision efficiency is a balance between
  - – Attractive van der Waals forces
  - – Repulsive forces
    - Electrostatic
    - Shear
- A global collision efficiency coefficient is considered

$$\alpha_g = \alpha_E - \alpha_E \alpha_S + \alpha_S$$



Results: BaSO4 precipitation model

C_{BaCl_2}=100 kmol/m^3, $C_{Na_2SO_4}$=100 kmol/m^3
$\alpha_g = 1$



C_{BaCl_2}=800 kmol/m^3, $C_{Na_2SO_4}$=100 kmol/m^3
$\alpha_g = 0$

Flow field modeling

- With the Large Eddy Simulation approach a filter is applied to the Navier-Stokes equations
- The filtered velocity field is obtained

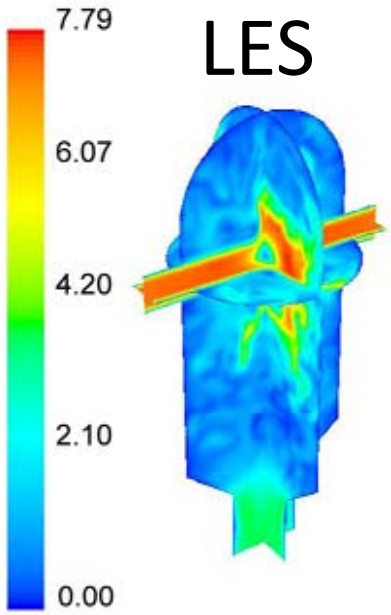
$$\overline{\mathbf{U}}(\mathbf{x},t) = \int G(\mathbf{r},\mathbf{x})\,\mathbf{U}(\mathbf{x}-\mathbf{r},t)\,d\mathbf{r}$$

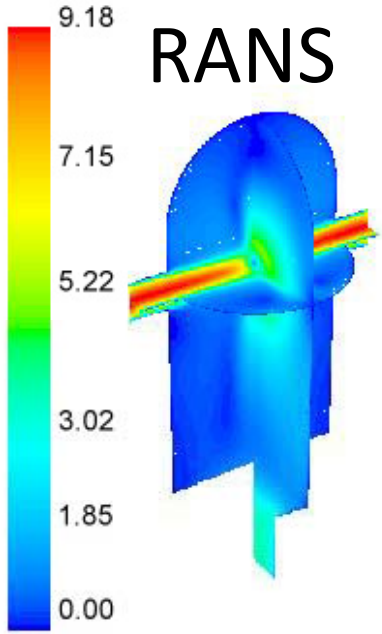
- The bigger scales of the flow, or large eddies are solved exactly, while the smaller scales are modelled with a Subgrid Scale Model
- For example the Smagorinsky-Lilly

$$\tau_{ij}^{r} = -2\nu_r \overline{S_{ij}} = -2 l_S^2 \overline{S} = -2\left(C_S \Delta\right)^2 \overline{S}$$

- The Reynolds Averaged Navier Stokes approach averages in time Navier-Stokes equations and the time averaged velocity field results

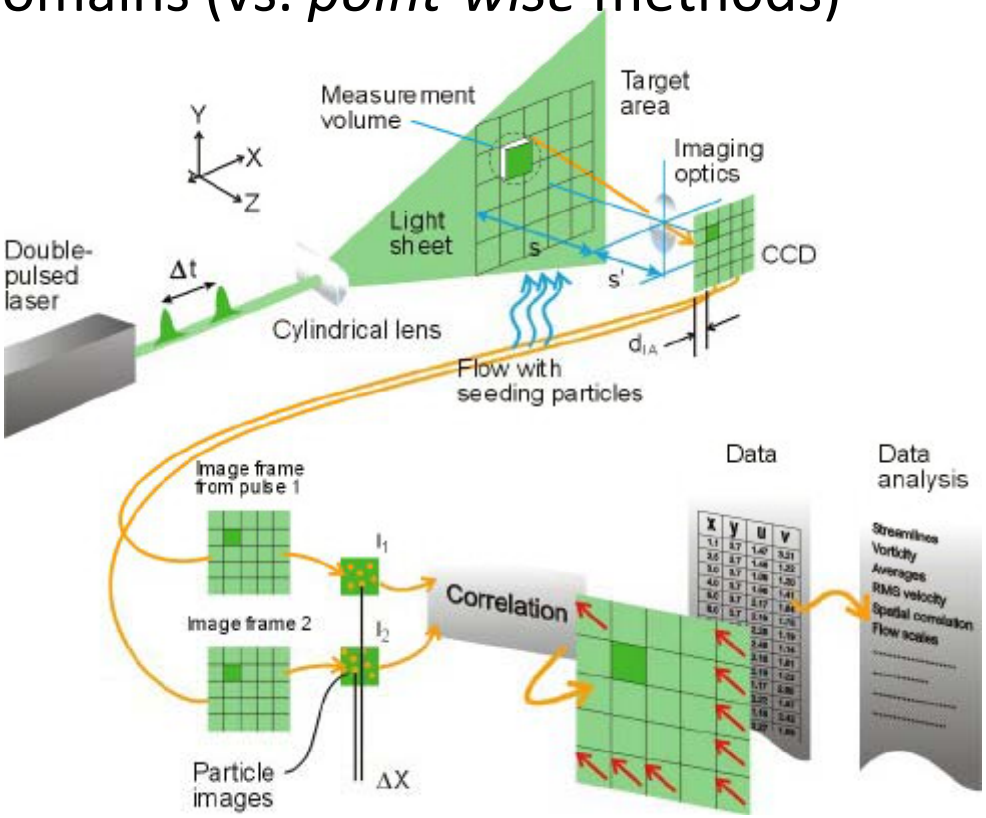
$$\langle \mathbf{U} \rangle(\mathbf{x}) = \frac{1}{T}\int_0^T \mathbf{U}(\mathbf{x},\mathrm{t})\ dt$$





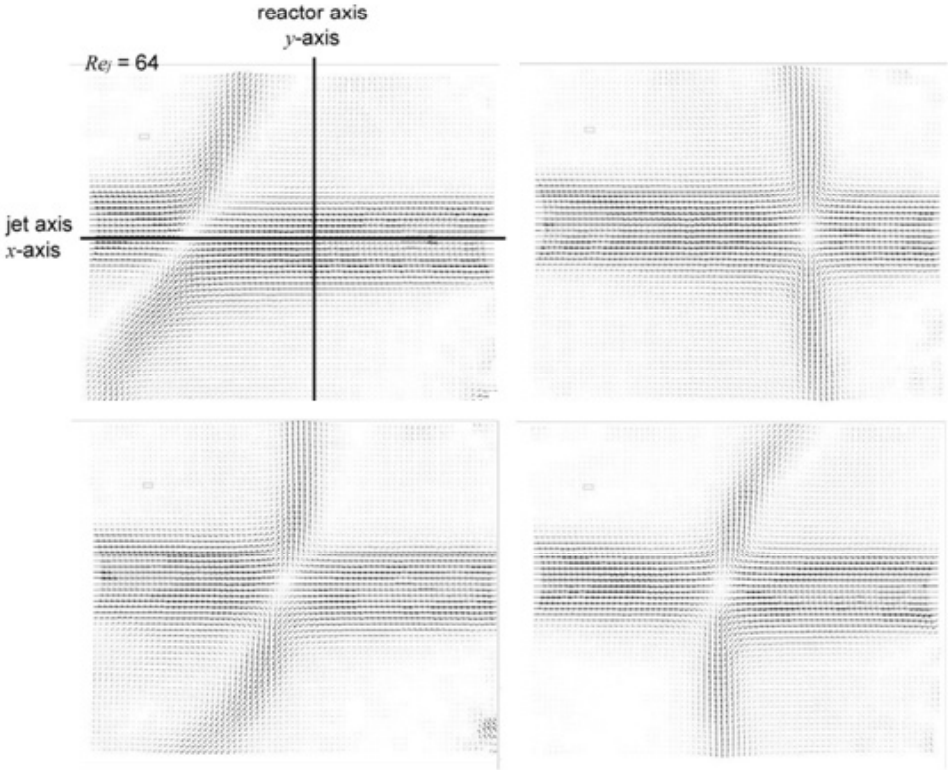
Micro Particle Image Velocimetry

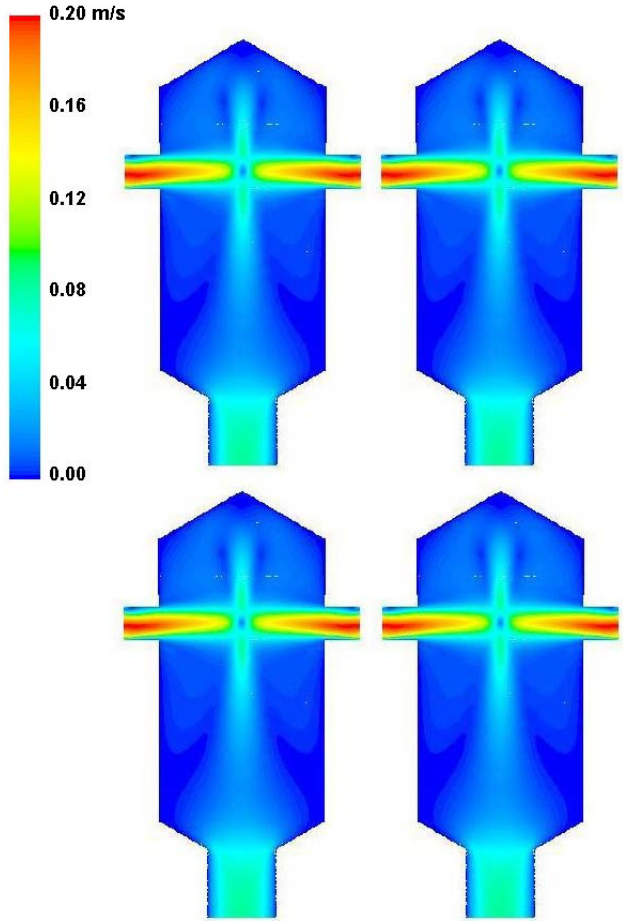
- PIV provides *instantaneous* velocity fields over *global* domains (vs. *point-wise* methods)



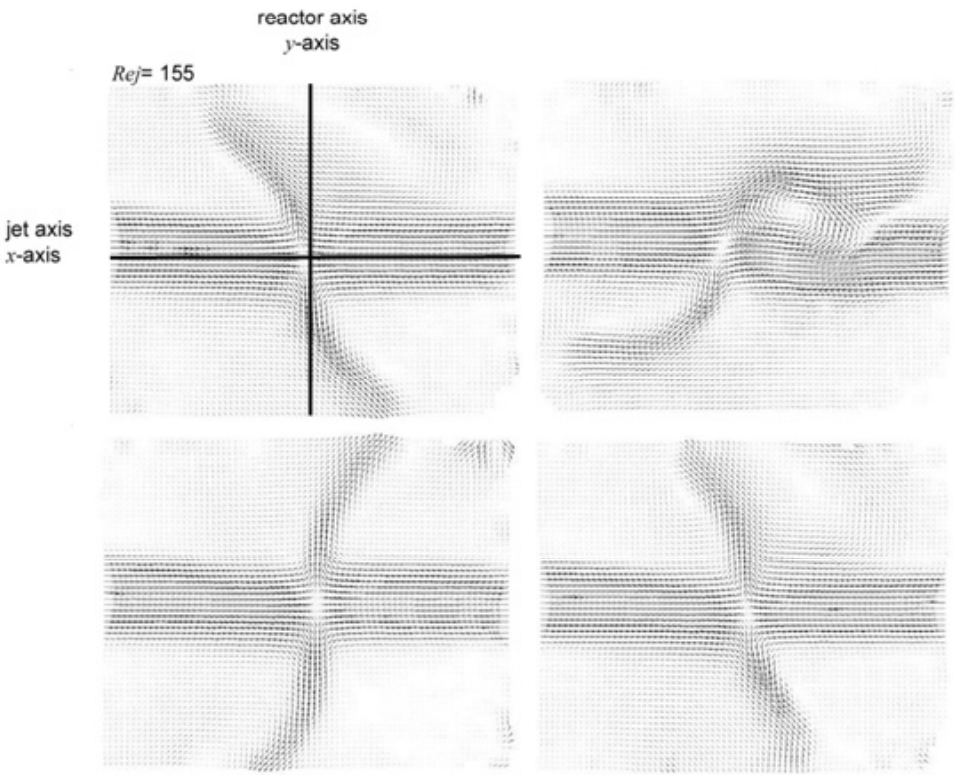
- Displacement of particles $$D\left(\mathbf{X};t',t''\right)=\int_{t'}^{t''} v\left[\mathbf{X}\left(t\right),t\right]dt$$

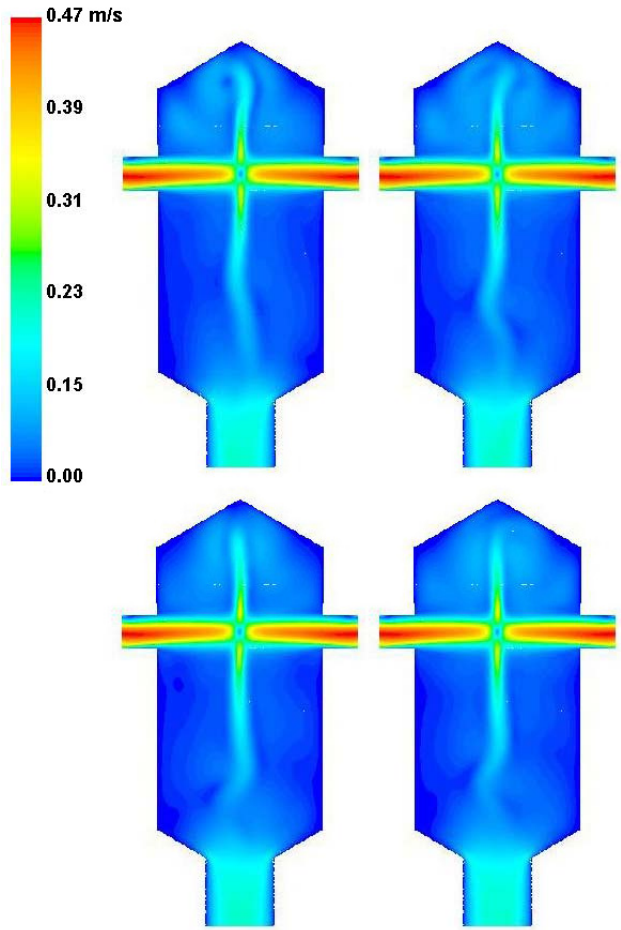
μPIV and LES results – $Re_j = 64$



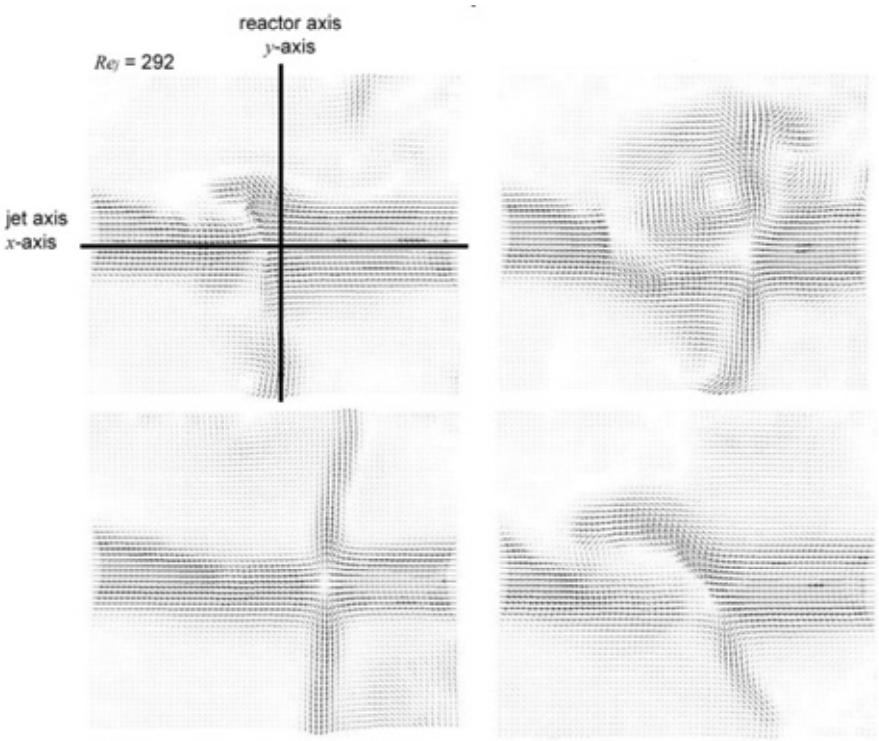


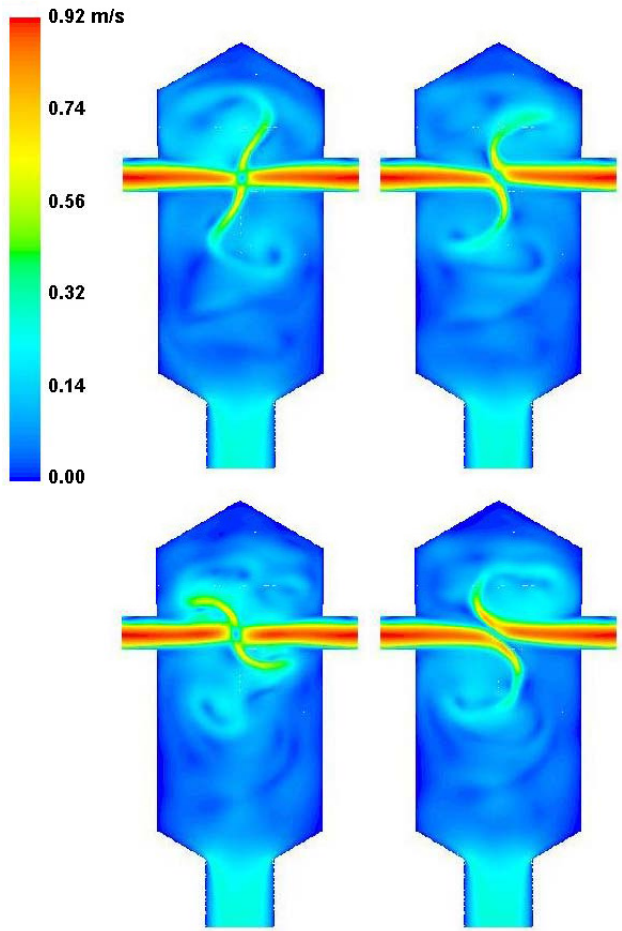
μPIV and LES results – Re_j = 155



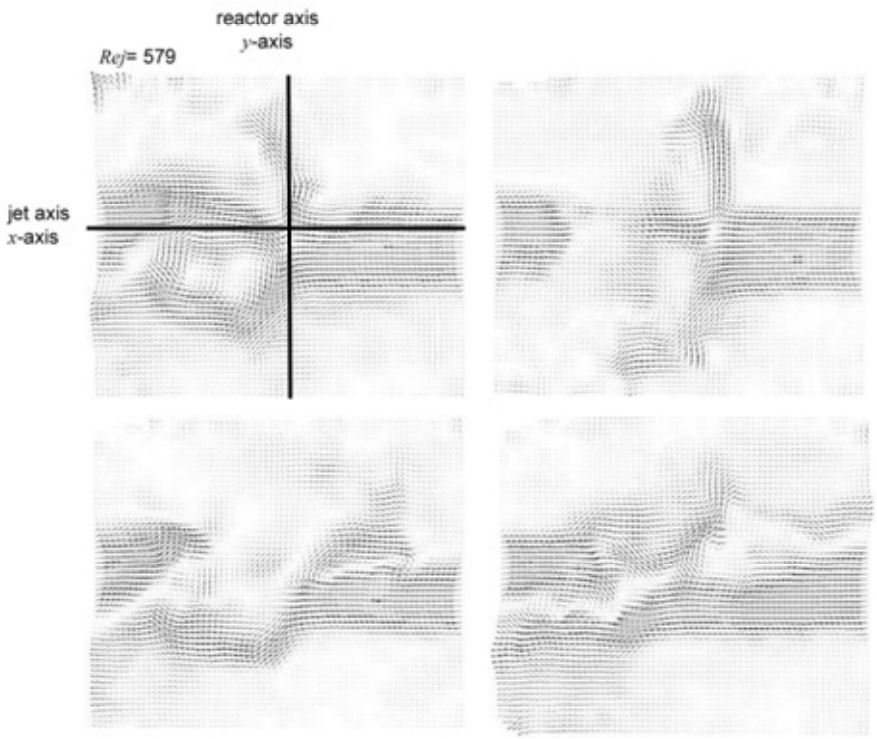


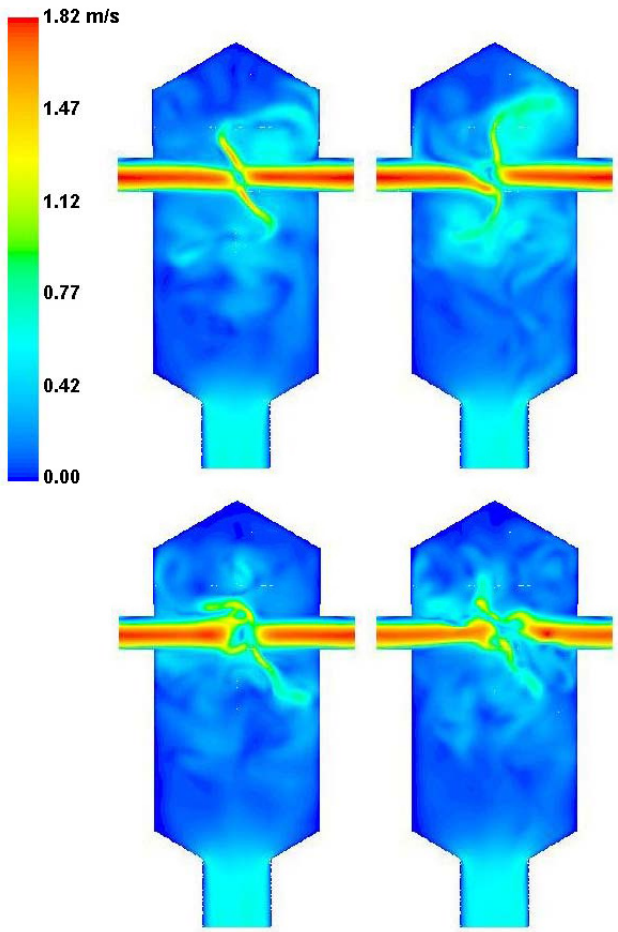
μPIV and LES results – Re_j = 292



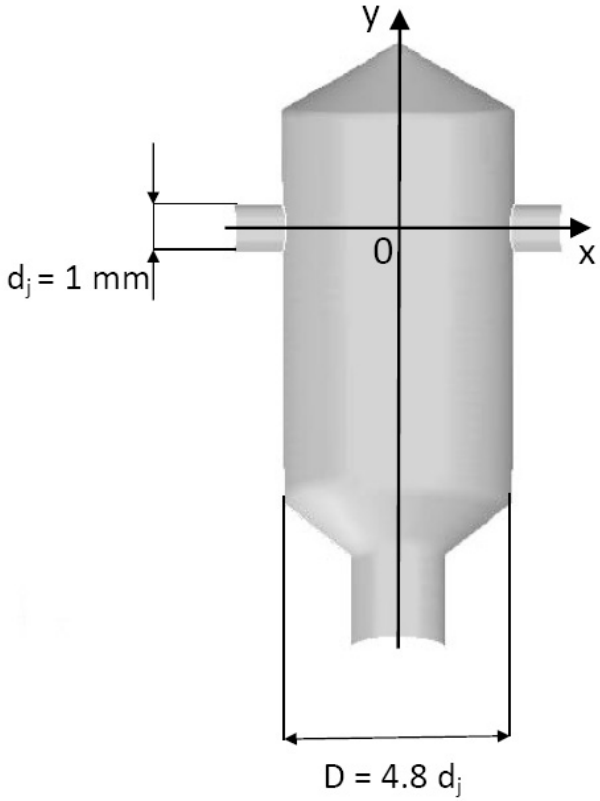


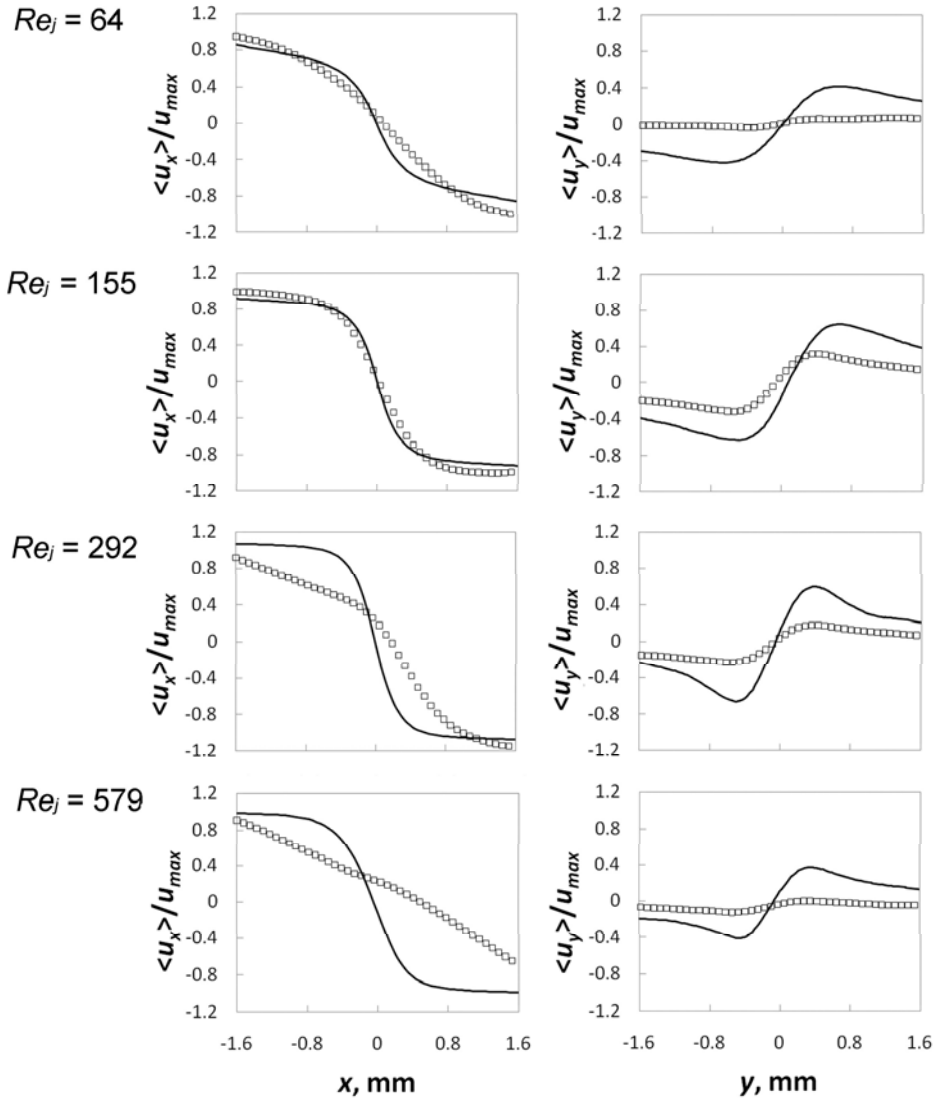
μPIV and LES results – Re_j = 579



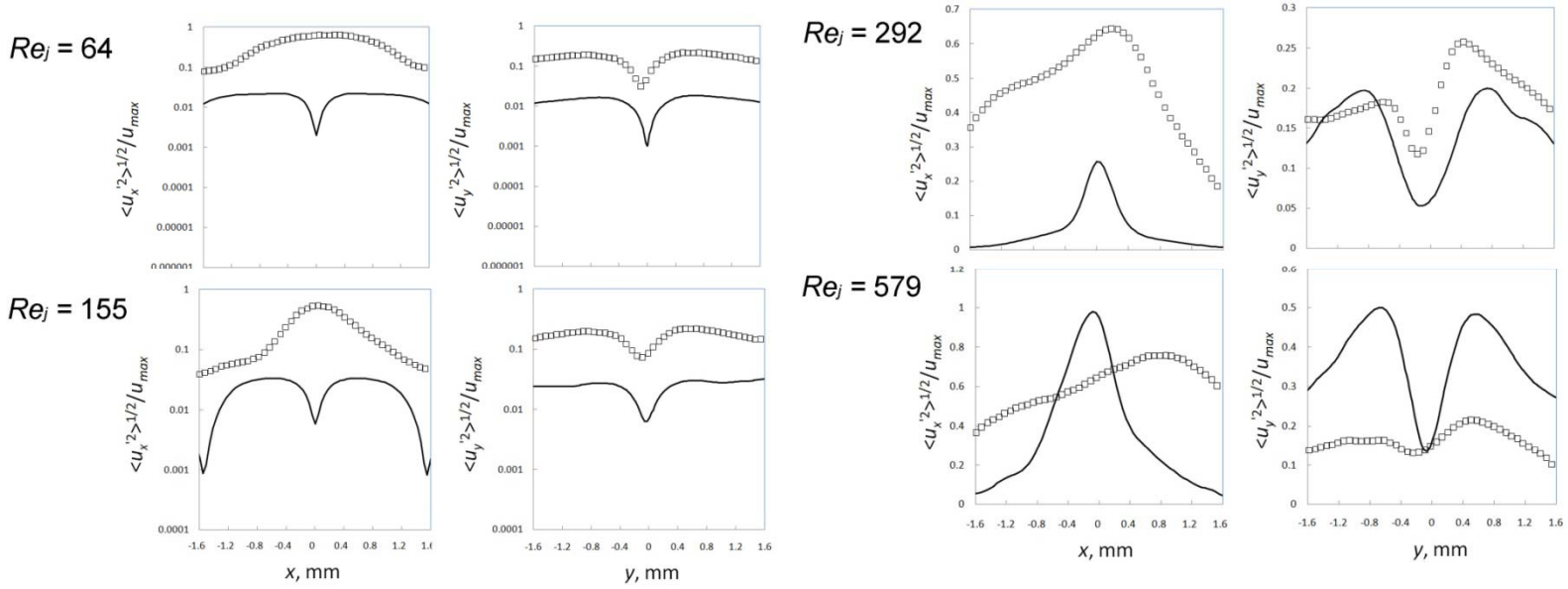


Quantitative comparison: time averaged velocity





Quantitative comparison: RMS velocity



Conclusions and next steps

- A fully predictive model was developed to describe mixing and precipitation
- In the aggregation term a global collision efficiency is considered in order to take into account the effect of repulsive forces of electrostatic and hydrodynamic nature
- The model was applied to the precipitation of $BaSO_4$, good agreement with experimental data was found
- μPIV measurements and LES prediction of the flow field in a CIJR at four operating conditions (Re_j = 64, 155, 292, 579) were compared
- The flow field in the CIJR was proven by means of experiments to be non-symmetrical and highly unsteady, and LES were able to predict these main features of the flow
- Quantitative comparisons in terms of first and second order statistics are satisfactory, also considering the difficulties in matching the inlet conditions between experiments and simulations, the issues related to μPIV resolution, and the (numerical diffusion)
- Next steps are the application of the precipitation model to PCL precipitation via solvent displacement process and the implementation of the mixing and reactive model on LES

Acknowledgements

- Federica Lince for experiments on PCL precipitation
- The Italian Ministry for University and Research for the fellowship of one of the authors (E. Gavi)

Thank you for your attention

Any question?