CoMFRE Multiphase Flow Research

IOWA STATE UNIVERSITY

A quadrature-based CFD model for turbulent reacting flows coupled with population balance

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Acknowledgements

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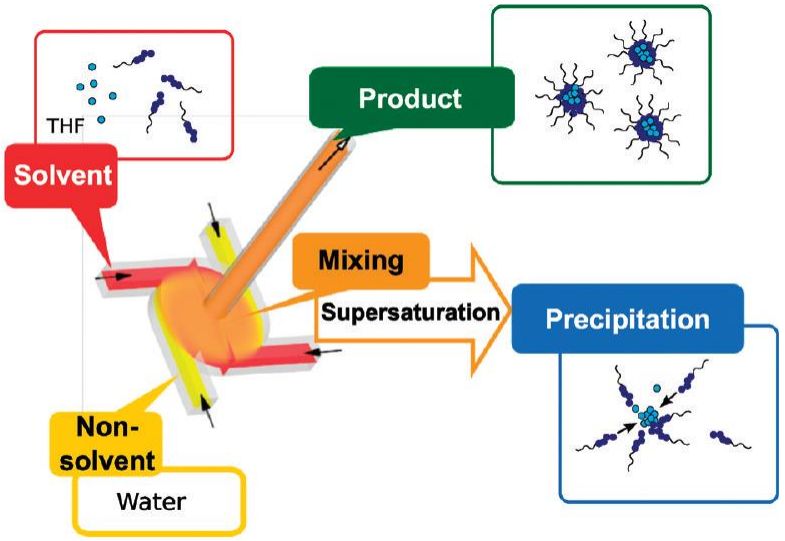
3. PDF transport models for turbulent reacting flows
4. Mixing and reaction in the MIVR
5. Population balance for flash-nanoprecipitation in the MIVR
6. Conclusions



J. C. Cheng and R. O. Fox, "Kinetic Modeling of Nanoprecipitation using CFD Coupled with a Population Balance," Industrial & Engineering Chemistry Research, vol. 49, pp. 10651-10662, Nov 3 2010

Multi inlet vortex reactor (MIVR)

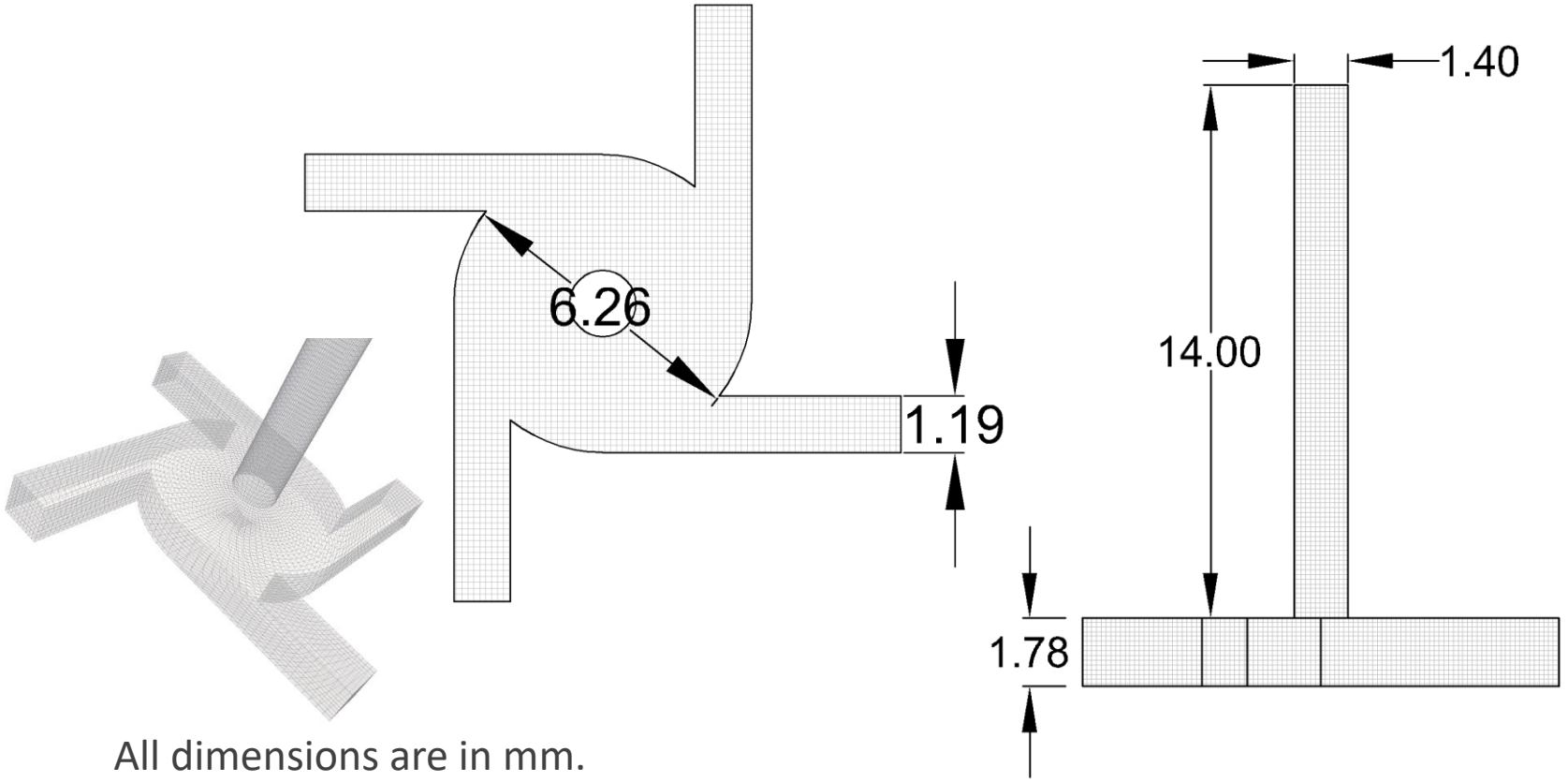
The multi-inlet vortex reactor (MIVR) is used for flash nanoprecipitation to manufacture functional nanoparticles:

- **Electronics**: provided a powerful path to developing small and powerful electronic components.
- **Drug Delivery**: nano-sized micelles accumulate in tumors via the enhanced permeability and retention effect.
  - **Nanoparticles doped on hydrogels for cancer treatment**

The MIVR achieves fast mixing by inducing turbulent swirling flow from four inlet streams.

A reliable numerical simulation is required to understand the fluid dynamics of the MIVR and to optimize its design and performance.

Reference Multi Inlet Vortex Reactor

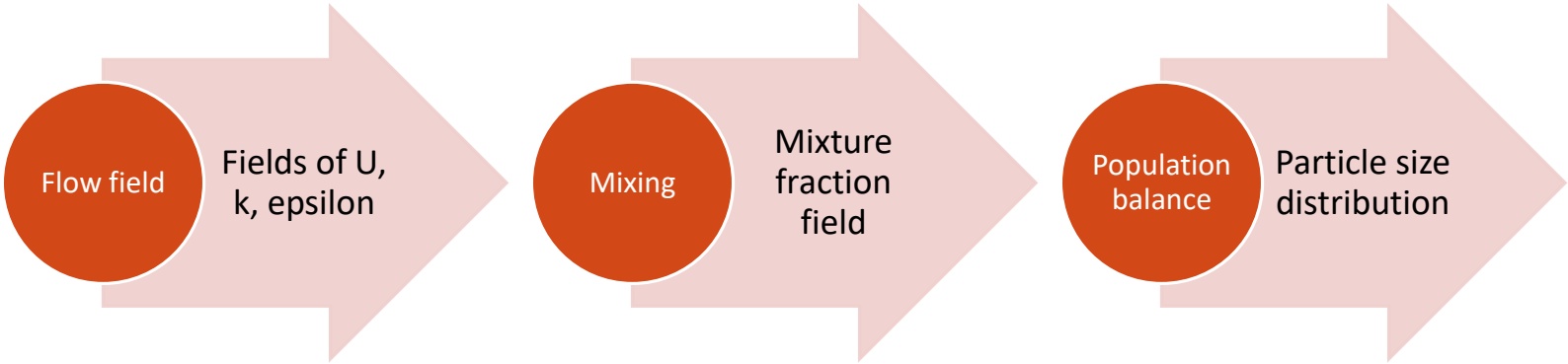


All dimensions are in mm.

Y. Shi, J. C. Cheng, R. O. Fox and M. G. Olsen, "Measurements of turbulence in a microscale multi-inlet vortex nanoprecipitation reactor" *Journal of Micromechanics and Microengineering,* vol. 23, 075005(10pp), 2013.

Simulation workflow

A sequential workflow is used to investigate the MIVR:

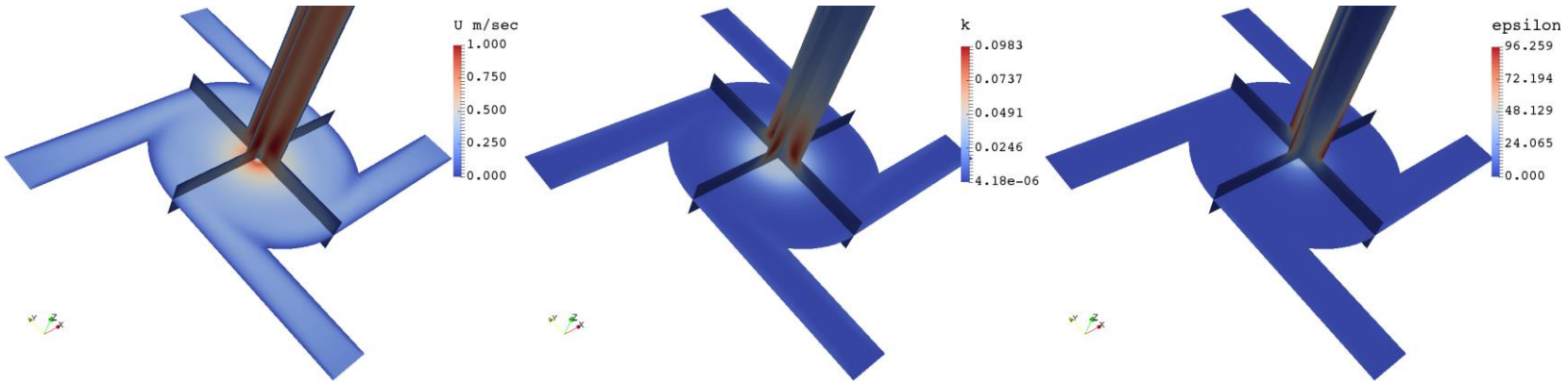


Assumptions

- Particles have small Stokes number and do not affect the fluid motion
- The flash nano-precipitation does not significantly affect mixing

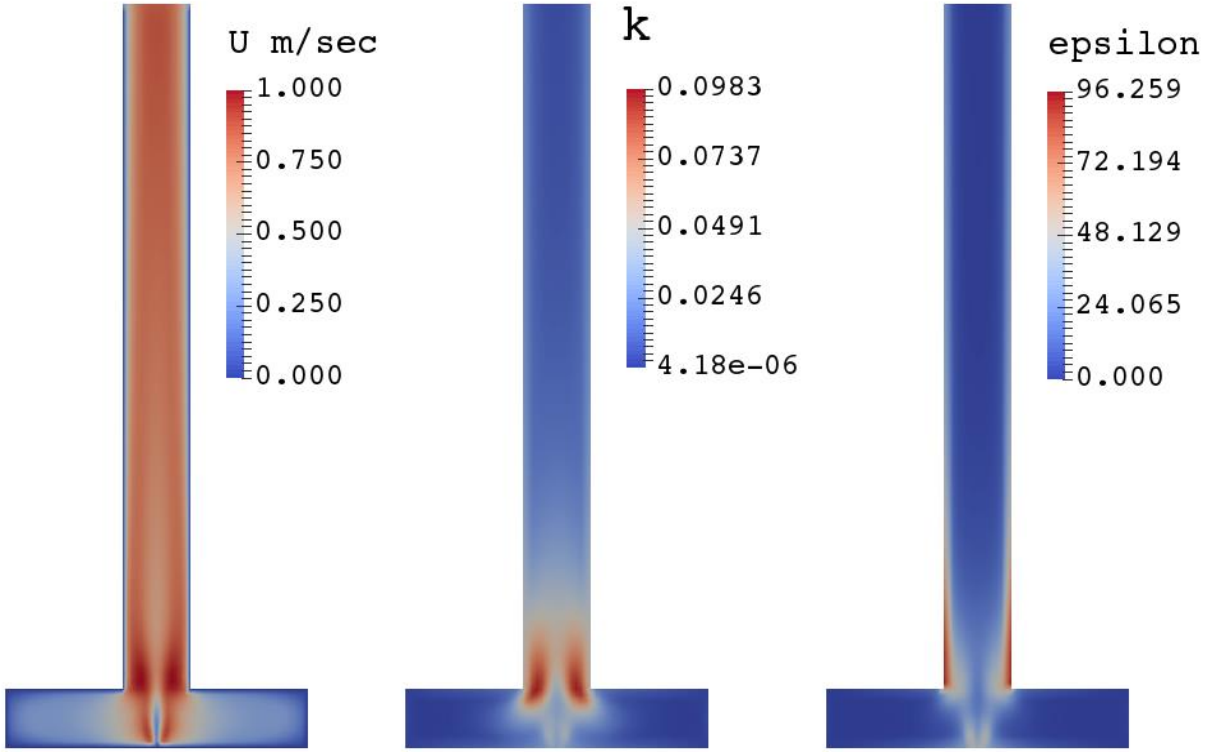
Flow field

- Incompressible steady-state RANS simulation (simpleFoam solver in OpenFOAM®)
- MIVR generates swirling flow, with higher turbulent intensity in the center of the mixing chamber
- Most of the fluid-particle interactions happen in the center of chamber and thus it is the place where the turbulent dissipation (ε) is higher.



Steady state solution of the velocity (left), turbulent kinetic (middle) and turbulent dissipation (right) of the flow.

Flow field and turbulent quantities



Steady state solution of the velocity (left), turbulent kinetic (middle) and turbulent dissipation (right) of the flow.

Reactive mixing modeling

We consider the evolution equation for the joint composition PDF $f(\boldsymbol{\phi}, \mathbf{x}, t)$:

$$\overbrace{\frac{\partial f_\phi}{\partial t}}^{\text{rate of change}} + \overbrace{\langle U_i \rangle \frac{\partial f_\phi}{\partial x_i}}^{\text{macromixing}} - \overbrace{\frac{\partial}{\partial x_i}\left(\Gamma_T \frac{\partial f_\phi}{\partial x_i}\right)}^{\text{mesomixing}} = -\frac{\partial}{\partial \psi_i}\left[\left(\frac{\varepsilon_\phi}{\langle \phi'^2 \rangle}(\langle \phi_i \rangle - \psi_i) + S_i(\psi)\right) f_\phi\right]$$

Closed by gradient-diffusion model

where

- ϕ is the passive scalar
- $\langle \phi'^2 \rangle$ is the scalar variance
- ε_ϕ is the dissipation factor
- $\langle U_i \rangle$ is the mean velocity
- Γ_T is the turbulent diffusivity
- t is time

Interaction by Exchange with the Mean mixing model (Fox, 2003)

Source term due to reaction

Chemical kinetics

We consider a simple case of two competitive consecutive reactions

$$A + B \xrightarrow{k_1} R$$ Fast reaction

$$B + R \xrightarrow{k_2} S$$ Slower reaction

where

- R is the desired product
- S is the byproduct
- $\frac{k_1}{k_2} = O(10^3)$

Rewrite PDF in terms of

- Mixture fraction ξ
- Reaction progress variables Y_1, Y_2

$$f(\boldsymbol{\phi}, \mathbf{x}, t) \rightarrow f(\xi, Y_1, Y_2, \mathbf{x}, t)$$

$$\xi_{st} = \frac{c_{A_0}}{c_{A_0} + c_{B_0}}$$

$$c_A = c_{A_0}[1 - \xi - (1 - \xi_{\mathrm{st}})Y_1]$$
$$c_B = c_{B_0}[\xi - \xi_{\mathrm{st}}(Y_1 + Y_2)]$$
$$c_R = c_{B_0}\xi_{\mathrm{st}}(Y_1 - Y_2)$$
$$c_S = c_{B_0}\xi_{\mathrm{st}}Y_2$$

Quadrature-based moment methods

The evolution equation for the joint composition PDF of mixture fraction, progress variable one and two $f(\xi, Y_1, Y_2;\ \mathbf{x}, t)$:

$$\frac{\partial f}{\partial t} + \langle U_i \rangle \frac{\partial f}{\partial x_i} - \frac{\partial}{\partial x_i}\left(\Gamma_T \frac{\partial f}{\partial x_i}\right) = -\frac{\partial}{\partial \xi}\left[\left(\frac{\varepsilon_\xi}{\langle \xi'^2 \rangle}(\langle \xi \rangle - \xi) + S(\xi)\right) f\right]$$
$$-\frac{\partial}{\partial Y_1}\left[\left(\frac{\varepsilon_{Y_1}}{\langle Y_1'^2 \rangle}(\langle Y_1 \rangle - Y_1) + S(Y_1)\right) f\right]$$
$$-\frac{\partial}{\partial Y_2}\left[\left(\frac{\varepsilon_{Y_2}}{\langle Y_2'^2 \rangle}(\langle Y_2 \rangle - Y_2) + S(Y_2)\right) f\right]$$

Apply moment definition ⇓ $M_{njk} = \int \xi^n Y_1^j Y_2^k f \mathrm{d}\xi \mathrm{d}Y_1 \mathrm{d}Y_2$

Finite set of moment transport equations

$$\frac{\partial M_{njk}}{\partial t} + \nabla \cdot \left(\mathbf{U} M_{njk}\right) - \nabla \cdot \left(\Gamma_T \nabla M_{njk}\right) = h \Rightarrow$$

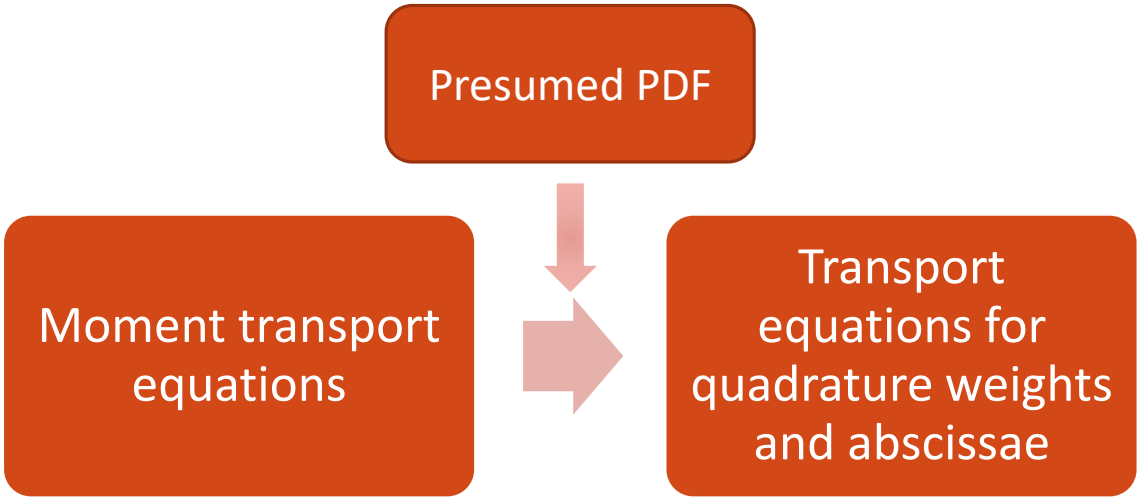
Closure problem

Direct quadrature method of moments - DQMOM

The PDF is presumed to have the form:

$$f(\phi, x, t) = \sum_{\alpha=1}^{N} w_\alpha \delta(\phi - \phi_\alpha)$$

where w_α and ϕ_α are quadrature weights and abscissae obtained from the transported moments by means of a moment inversion algorithm



Challenges with DQMOM

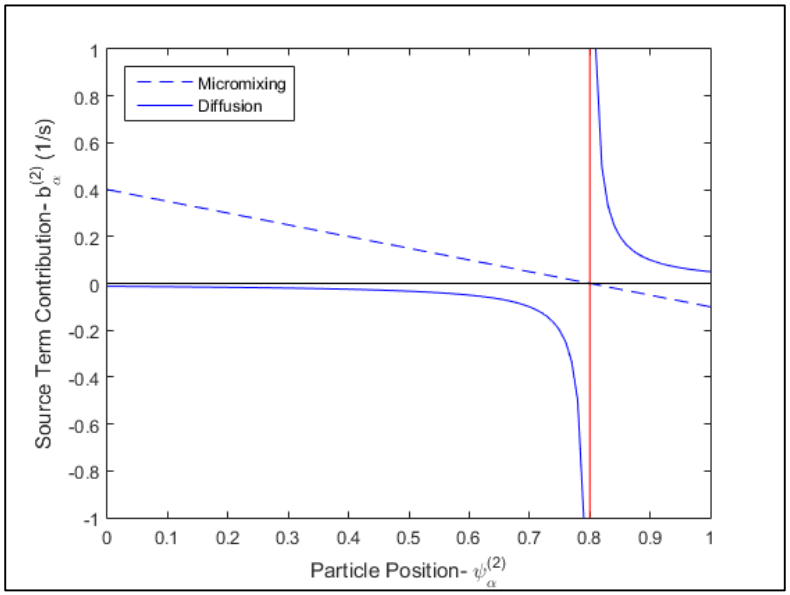
Singularity in the correction terms

- Numerical instability if untreated
- Need of smoothing functions (Akroyd et al., Chem. Eng. Sci, 2010)
- Removal of correction terms (but it leads to incorrect predictions of the variance of the mixture fraction!)

Transports non-conservative quantities (weights and abscissae)

CQMOM:

- Avoids singularities
- Transports conserved quantities (moments) rather than non-conservative quantities



J. Akroyd, A. J. Smith, L. R. McGlashan, and M. Kraft, "Numerical investigation of DQMoM-IEM as a turbulent reaction closure," Chemical Engineering Science, vol. 65, pp. 1915-1924, Mar 15 2010.

Conditional quadrature method of moments

We rewrite the joint composition PDF in terms of conditional PDFs:

$$f(\xi, Y_1, Y_2) = f(Y_2|\xi, Y_1) f(\xi, Y_1) = f(Y_2|\xi, Y_1) f(Y_1|\xi) f(\xi)$$

we then consider the conditional moments

$$\left\langle Y_1^j \right\rangle (\xi) \stackrel{\text{def}}{=} \int Y_1^j f(Y_1|\xi) \mathrm{d}Y_1$$

$$\left\langle Y_2^k \right\rangle (\xi, Y_1) \stackrel{\text{def}}{=} \int Y_2^k f(Y_2|\xi, Y_1) \mathrm{d}Y_2$$

and we represent the moments of PDF as

$$M_{njk}(\mathbf{x}, t) = \iiint \xi^n Y_1^j Y_2^k f(\xi, Y_1, Y_2; \mathbf{x}, t) \mathrm{d}\xi \ \mathrm{d}Y_1 \ \mathrm{d}Y_2$$

Conditional quadrature method of moments

We represent the PDF as (assuming one node for Y_1 and Y_2):

$$f(\xi, Y_1, Y_2; \mathbf{x}, t) = \sum_{\alpha=1}^{\mathrm{N}} w_\alpha \delta(\xi - \xi_\alpha)\delta\left(Y_1 - Y_{1_\alpha}\right)\delta\left(Y_2 - Y_{2_\alpha}\right)$$

and we represent the moments of PDF as:

$$M_{njk}(\mathbf{x}, t) = \sum_{\alpha=1}^{\mathrm{N}} w_\alpha \xi_\alpha^n Y_{1_\alpha}^j Y_{2_\alpha}^k$$

We consider:

- Two quadrature nodes for the ξ direction
- One quadrature node for the Y_1 direction
- One quadrature node for the Y_2 direction

$M_{000}, M_{100}, M_{200}, M_{300}$

M_{010}, M_{110}

M_{001}, M_{011}

Moment transport equations in CQMOM

$$\frac{\partial M_{njk}}{\partial t} + \nabla \cdot \left(\mathbf{U} M_{njk}\right) - \nabla \cdot \left(\Gamma_T \nabla M_{njk}\right)$$

$$= \frac{n\varepsilon_\xi}{\langle \xi'^2 \rangle}\left(M_{n-1jk} M_{100} - M_{njk}\right)$$

$$+ \sum_{\alpha=1}^{N} w_\alpha R_{1\alpha}\left(j \xi_\alpha^n Y_{1_\alpha}^{j-1} Y_{2_\alpha}^k\right) + \sum_{\alpha=1}^{N} w_\alpha R_{2\alpha}\left(k \xi_\alpha^n Y_{1_\alpha}^{j} Y_{2_\alpha}^{k-1}\right)$$

Scale similarity

$$\frac{\varepsilon_\xi}{\langle \xi'^2 \rangle} = C_\xi \frac{\varepsilon}{k}$$

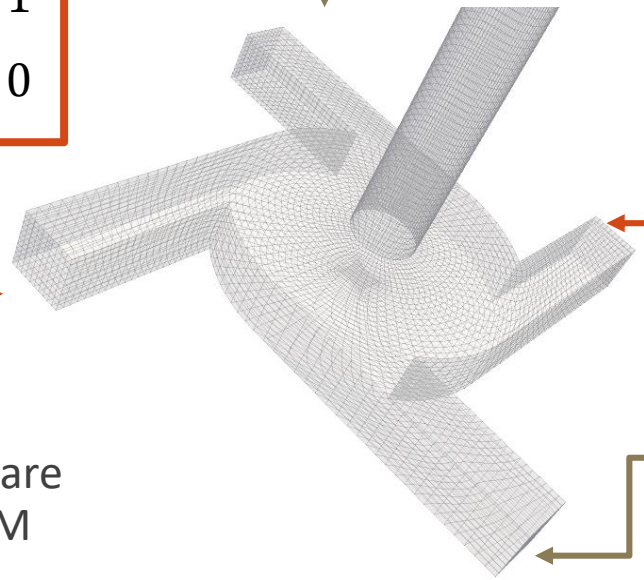
$$R_{1\alpha}(\xi_\alpha, Y_{1\alpha}, Y_{2\alpha}) = \xi_{st} k_1 c_{B_0}\left(\frac{1-\xi_\alpha}{1-\xi_{st}} - Y_{1\alpha}\right)\left(\frac{\xi_\alpha}{\xi_{st}} - Y_{1\alpha} - Y_{2\alpha}\right)$$

$$R_{2\alpha}(\xi_\alpha, Y_{1\alpha}, Y_{2\alpha}) = \xi_{st} k_2 c_{B_0}(Y_{1\alpha} - Y_{2\alpha})\left(\frac{\xi_\alpha}{\xi_{st}} - Y_{1\alpha} - Y_{2\alpha}\right)$$

Mixing - Simulation setup

Two opposing inlet streams for solvent

$$M_{000} = 1 \quad M_{100} = 1$$
$$M_{200} = 1 \quad M_{300} = 1$$
$$M_{010} = 0 \quad M_{110} = 1$$
$$M_{001} = 0 \quad M_{101} = 0$$



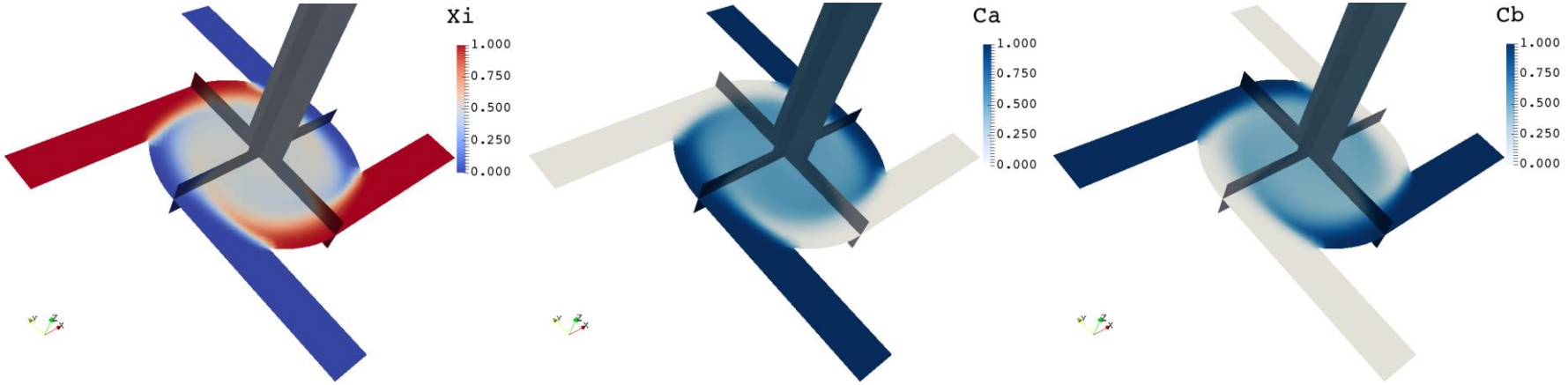
Two opposing inlet streams for nonsolvent

$$M_{000} = 1 \quad M_{100} = 0$$
$$M_{200} = 0 \quad M_{300} = 0$$
$$M_{010} = 0 \quad M_{110} = 1$$
$$M_{001} = 0 \quad M_{101} = 0$$

Mixing and reaction fields are obtained using OpenQBMM (www.openqbmm.org)

Pure mixing (no reaction)

- Mixture fraction represents the mixing progress.
- Two streams have $\langle \xi \rangle = 0$ and two other have $\langle \xi \rangle = 1$.
- Through micromixing, mixture fraction relaxes to value $\langle \xi \rangle = 0.5$.
- $\langle \xi \rangle = 0.5$ is when the simulation is fully converged.
- In FNP processes $\langle \xi \rangle$ is key, since the solvent and non-solvent should reach a specific ratio to precipitate.

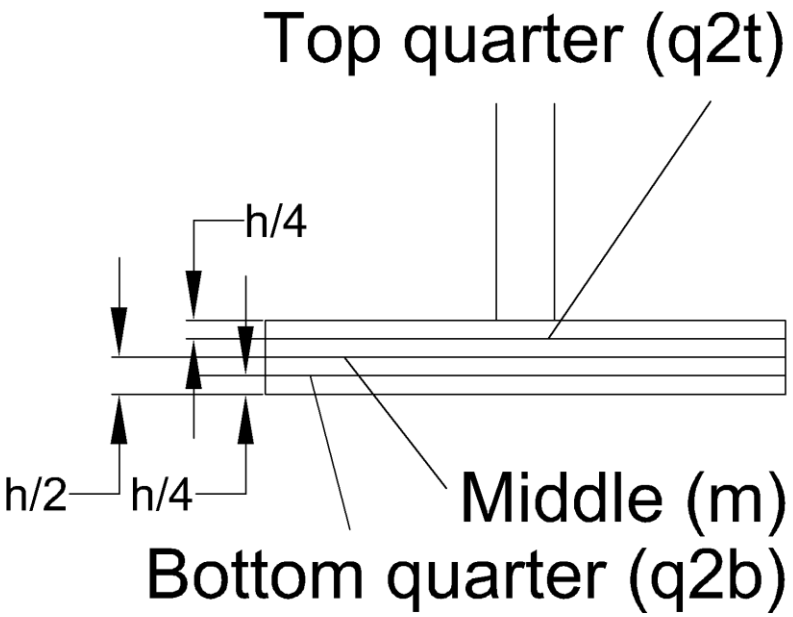


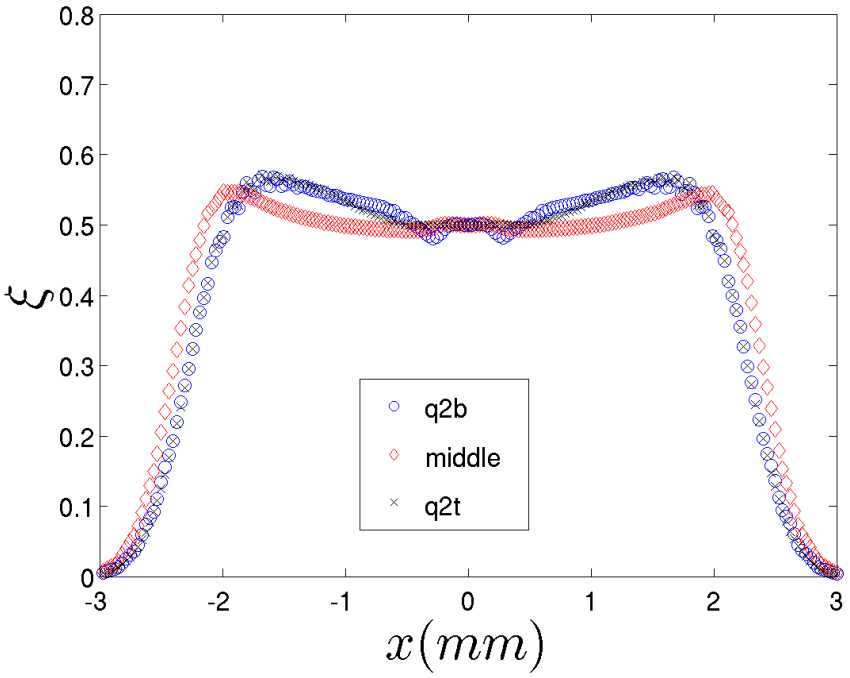
The mixture fraction (left), concentration A (middle), and concentration B (right).

Predicted mixture fraction

- The mean mixture fraction is defined as:

$$\langle \xi \rangle = M_1$$





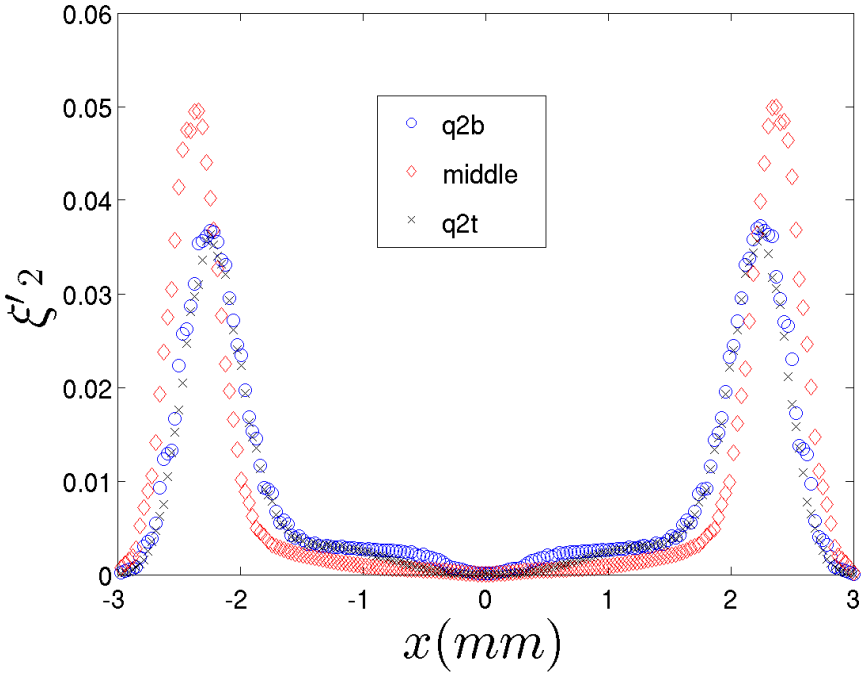
Mean mixture fraction inside the mixing chamber shown in three plates, middle, top quarter (q2t) and bottom quarter (q2b).

Predicted variation of mixture fraction

- The variance of the mixture fraction an be written as:

$$\langle \xi'^2 \rangle = M_2 - M_1^2$$

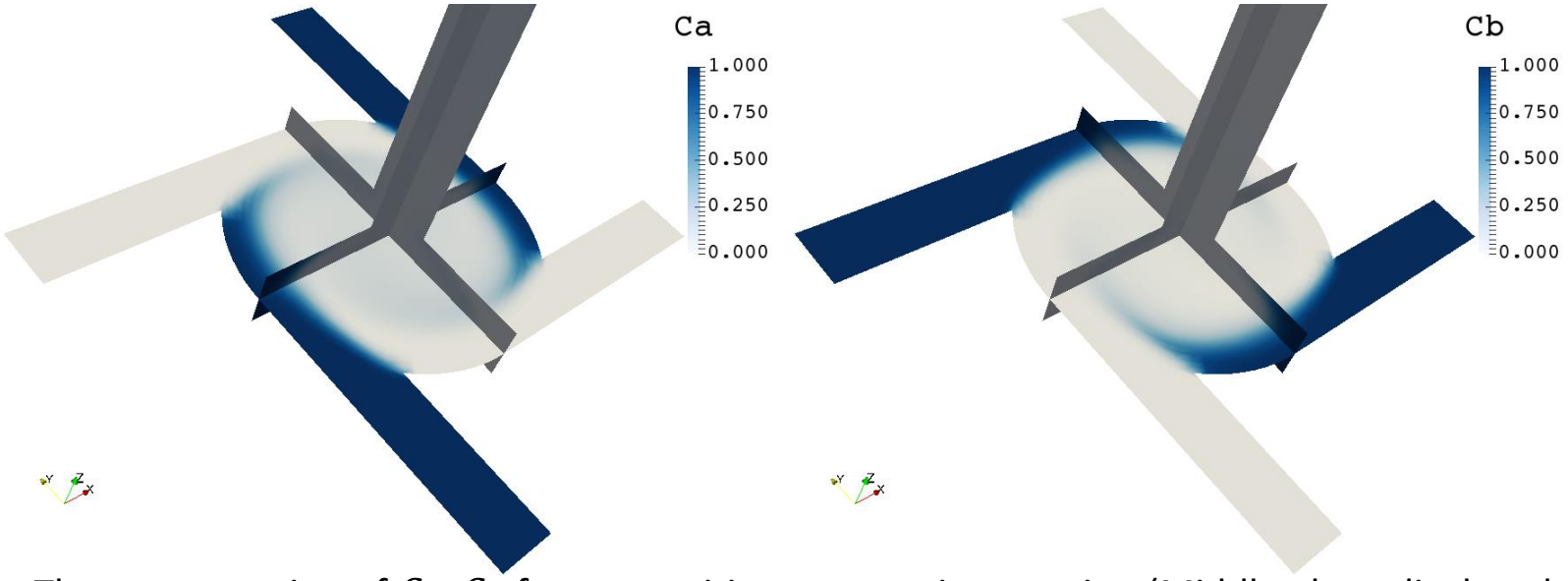
- $\langle \xi'^2 \rangle$ decays quickly after inlet streams enter the reactor.
- Variance is higher in the quarter top and quarter bottom planes compare to middle plate inside the mixing chamber.
- Higher variance is obtained at middle plate near to inlet streams.
- Since the flow is turbulent, the variation of mixture fraction is not big.



The variance inside the mixing chamber shown in three plates, middle, top quarter (q2t) and bottom quarter (q2b).

Mixing with competitive consecutive reaction

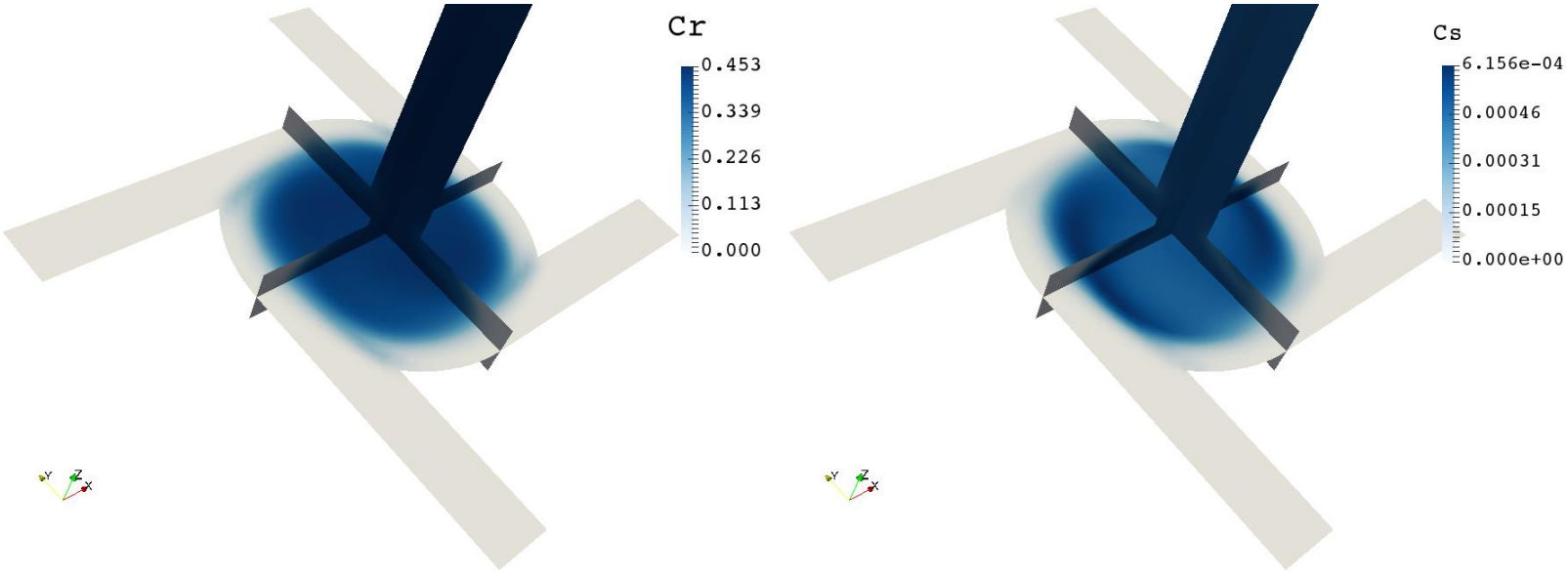
- Simulations show that mostly inside the mixing chamber, species B is consumed.
- The main reaction happens between A and B since the rate of their reaction is $O(1000)$ higher than the secondary reaction.



The concentration of C_A, C_B for competitive consecutive reaction (Middle plane displayed for the chamber).

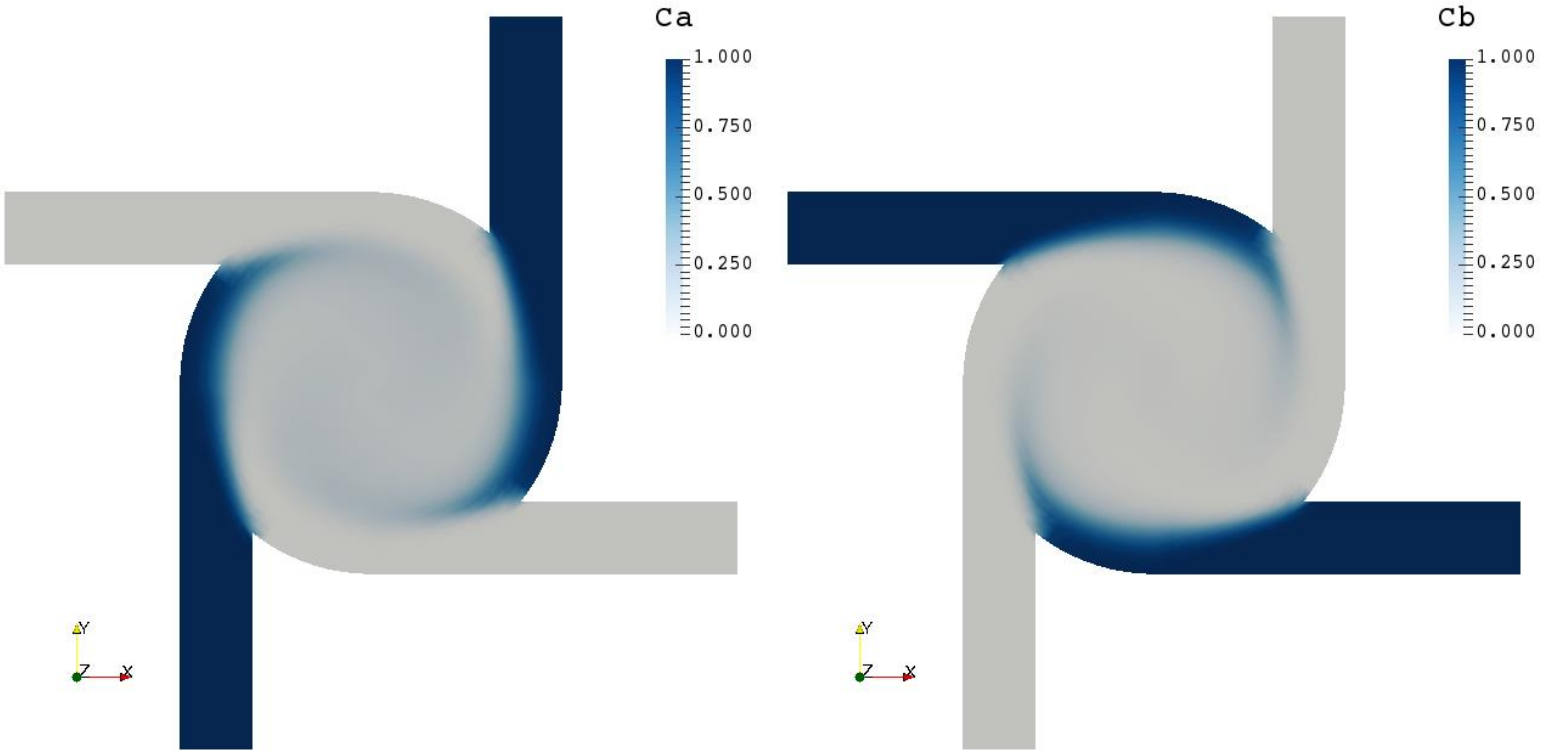
Mixing with competitive consecutive reaction

- The main product R is mostly produced inside the chamber and moves toward the exit.
- The byproduct S is produced due to the presence of R and B, when A is absent (mixing limitation).



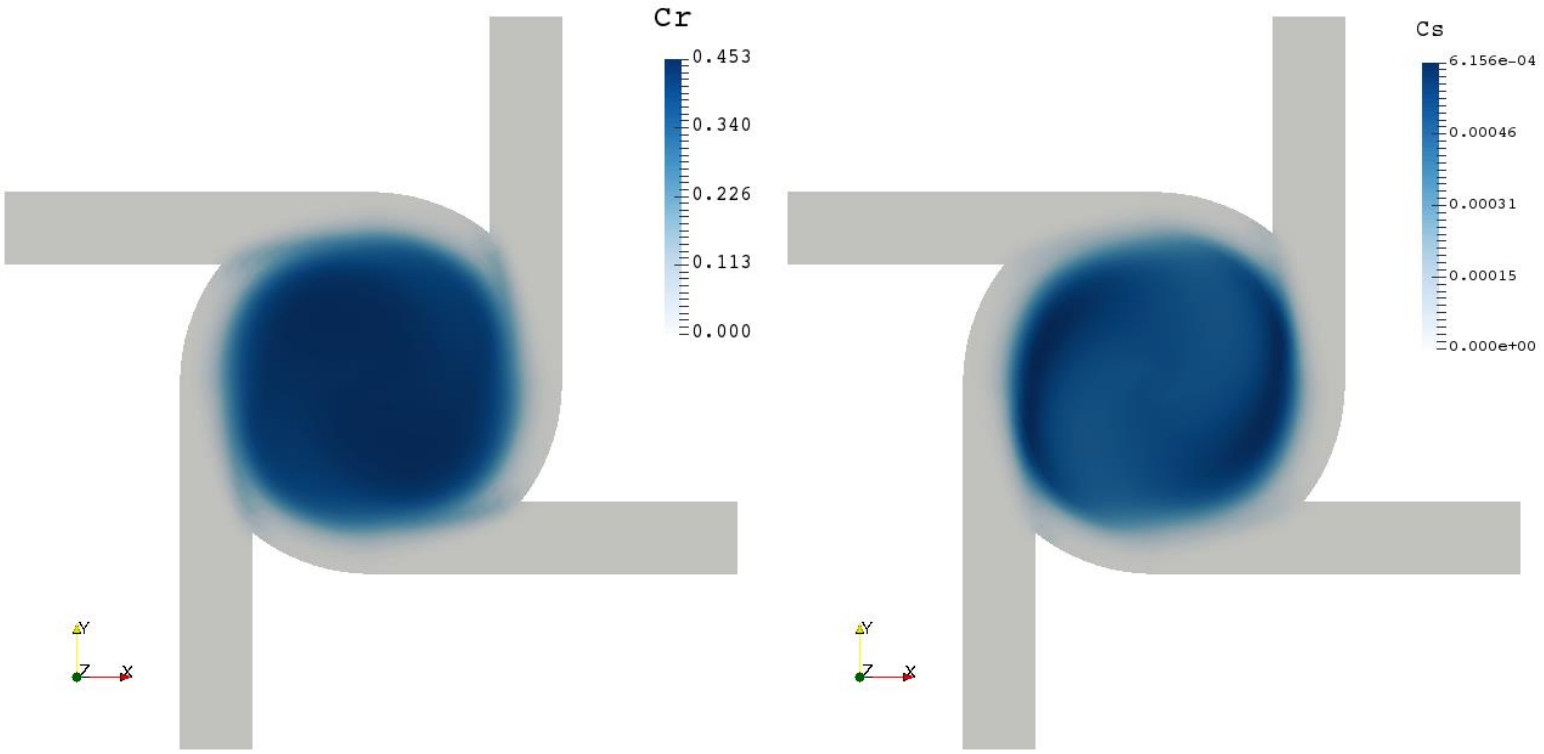
The concentration of product and bi-product for competitive consecutive reaction (Middle plane displayed for the chamber).

Mixing with competitive consecutive reaction



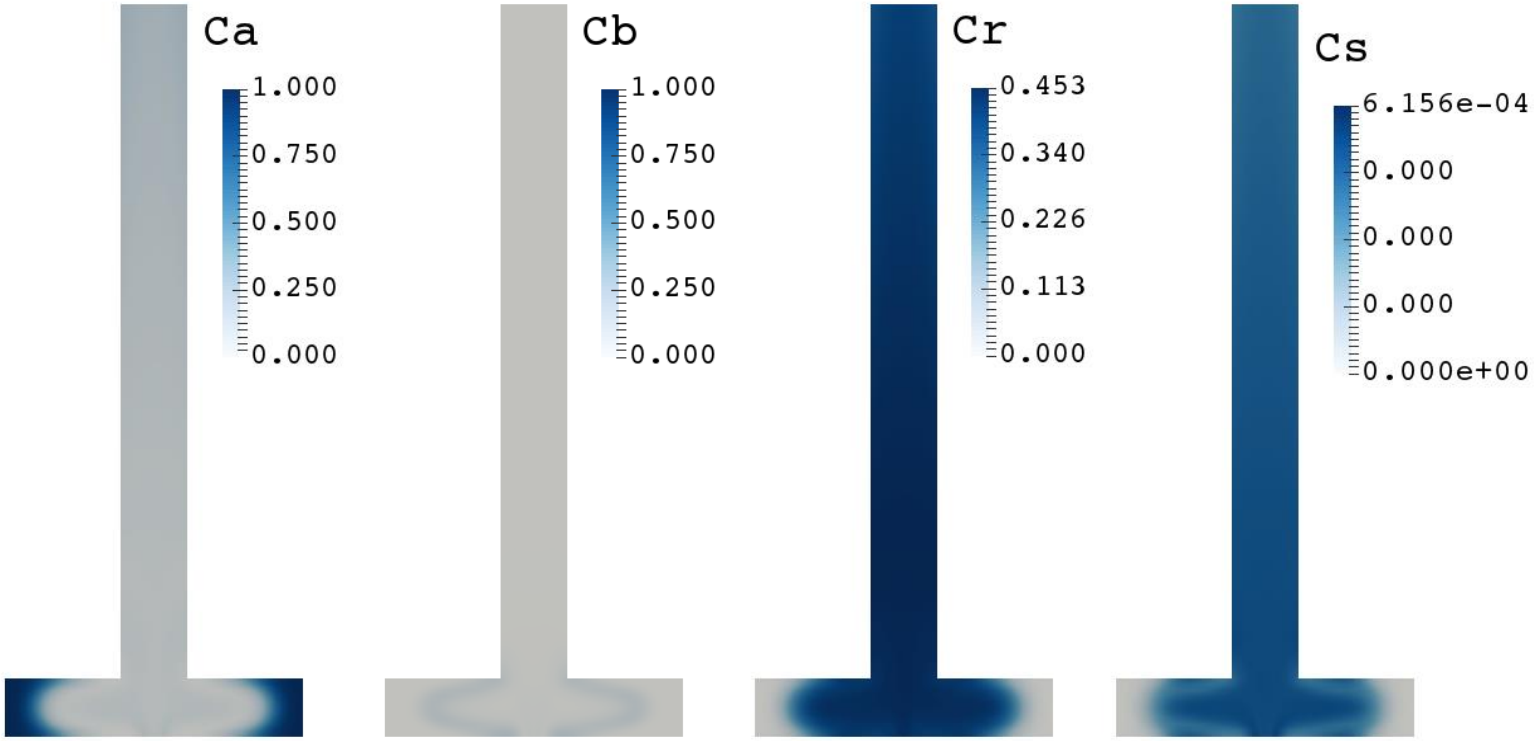
Concentration of C_A, C_B for competitive consecutive reaction (Middle plane displayed for the chamber).

Mixing with competitive consecutive reaction



The concentration of product and bi-product for competitive consecutive reaction (Middle plane displayed for the chamber).

Mixing with competitive consecutive reaction



The concentration of C_A, C_B, C_R, C_S for competitive consecutive reaction.

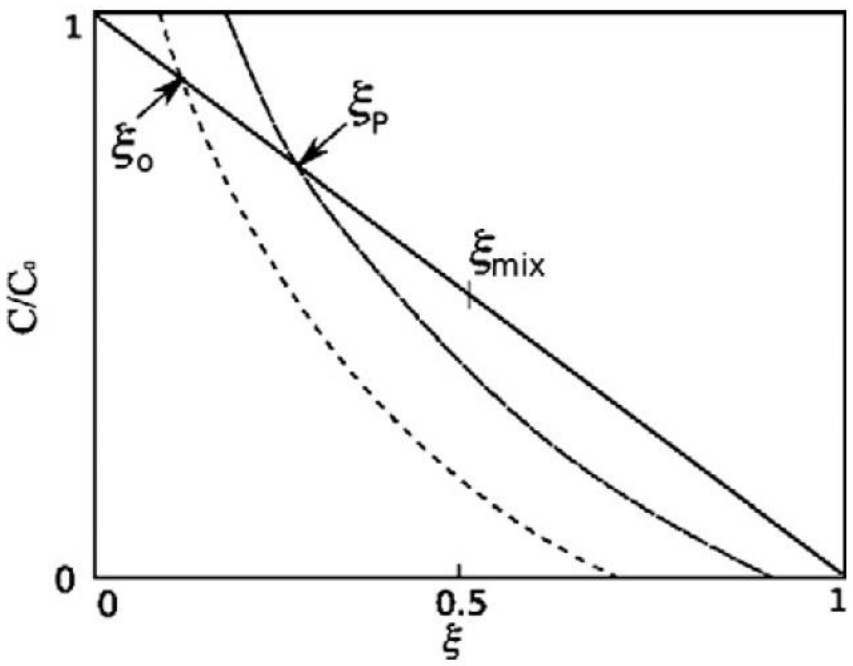
Flash nanoprecipitation solubility curve

The straight line indicates the mixing line between solvent and anti-solvent.

At ξ_{mix}, the two streams are well-mixed.

On the solubility curve, the aggregation kernel "activates" above ξ_p (solubility limit of polymer).

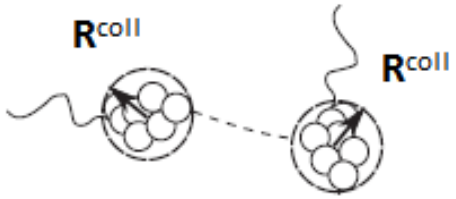
This phenomena is introduced to the equations as a Heaviside function (i.e. $\Theta_p = \Theta(\xi-\xi_p)$).



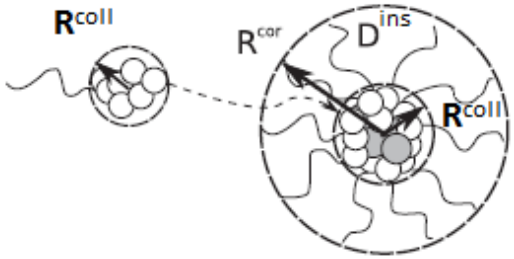
J. C. Cheng et al. "A competitive aggregation model for Flash NanoPrecipitation." *Journal of Colloid and Interface Science* ,vol. 351, pp. 330-342, Nov 15 2010.

Aggregation Mechanisms

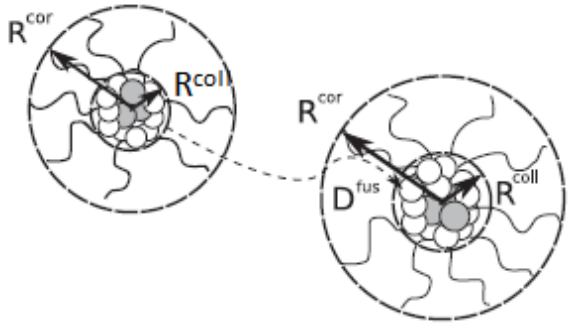
1) Free coupling



2) Unimer insertion



3) Large aggregate fusion



J. C. Cheng et al. “A competitive aggregation model for Flash NanoPrecipitation.” *Journal of Colloid and Interface Science* ,vol. 351, pp. 330-342, Nov 15 2010.

Aggregation Kernels

Free coupling

$$\beta_{1,1}^{\text{free}} = 4\pi\Theta_p(D_1 + D_1)\left(R_1^{\text{coll}} + R_1^{\text{coll}}\right)$$

Unimer insertion

$$\beta_{p,1}^{\text{ins}} = 4\pi\Theta_p A_{1,p}^{\text{ins}} \frac{\left(R_p^{\text{coll}} + R_1^{\text{coll}}\right)\left(R_p^{\text{coll}} + R_p^{\text{cor}} + R_1^{\text{coll}}\right)\left(D_p + D_1\right)D_{p,1}^{\text{ins}}}{\left(D_p + D_1\right)R_p^{\text{cor}} + \left(R_p^{\text{coll}} + R_1^{\text{coll}}\right)D_{p,1}^{\text{ins}}}$$

Large aggregate fusion

$$\beta_{p,1}^{\text{fus}} = 4\pi\Theta_p A_{1,p}^{\text{fus}} \frac{\left(R_p^{\text{coll}} + R_i^{\text{coll}}\right)\left(R_p^{\text{coll}} + R_p^{\text{cor}} + R_i^{\text{coll}} + R_i^{\text{cor}}\right)\left(D_p + D_i\right)D_{p,i}^{fus}}{\left(D_p + D_1\right)\left(R_p^{\text{cor}} + R_i^{\text{cor}}\right) + \left(R_p^{\text{coll}} + R_1^{\text{coll}}\right)D_{p,i}^{\text{fus}}}$$

PBE for flash-nanoprecipitation in the MIVR

The evolution equation for the population of polymers:

$$\frac{\partial f}{\partial t} + \langle \boldsymbol{U} \rangle \frac{\partial f}{\partial \boldsymbol{x}} - \frac{\partial}{\partial \boldsymbol{x}} \left(\Gamma_t \frac{\partial f}{\partial \boldsymbol{x}} \right)$$
$$= -\frac{\partial}{\partial \xi} \left[\frac{\varepsilon_\xi}{\langle \xi'^2 \rangle} (\langle \xi \rangle - \xi) f \right] - \frac{\partial}{\partial \underline{m}} \left[\frac{\varepsilon_\xi}{\langle \xi'^2 \rangle} (\langle \underline{m} \rangle - \underline{m}) f \right] - \frac{\partial}{\partial \underline{m}} \left[\underline{R}(\xi, \underline{m}) f \right]$$

where

- $f(\xi, L; \mathbf{x}, t)$ is the joint composition PDF of mixture fraction and PBE
- $\underline{R}(\xi, \underline{m}) = \frac{d\underline{m}}{dt}$ is change of moments in PBE given ξ
- $\underline{m}$ is the moment vector for PBE
- $\langle \boldsymbol{U} \rangle$ is the mean velocity
- Γ is the diffusion coefficient
- t is time

Apply moment definition

Finite set of moment transport equations

PBE for flash-nanoprecipitation in the MIVR

$$\underline{R}(\xi,\underline{m}) = \underbrace{\frac{L^2}{2}\int_0^L \frac{\beta\left((L^3-\lambda^3)^{1/3},\lambda\right)}{(L^3-\lambda^3)^{2/3}} f\left((L^3-\lambda^3)^{1/3};\mathbf{x},t\right) f(\lambda;\mathbf{x},t)\,d\lambda}_{\text{birth of particles due to aggregation}}$$

$$\underbrace{- f(L;\mathbf{x},t)\int_0^\infty \beta(L,\lambda) f(\lambda;\mathbf{x},t)\,d\lambda}_{\text{death of particles due to aggregation}}$$

Apply moment definition for PBE source terms

Aggregation kernel

$$\langle \underline{R}(\xi,\underline{m})\rangle = \frac{1}{2}\sum_{i=1}^{N} w_i \sum_{j=1}^{N} w_j (L_i^3 + L_j^3)^{k/3} \beta\left(L_i, L_j\right) - \sum_{i=1}^{N} w_i L_i^k \sum_{j=1}^{N} w_j \beta\left(L_i, L_j\right)$$

PBE for flash-nanoprecipitation in the MIVR

Moments of mixture fraction

$$\frac{\partial\langle\xi^k\rangle}{\partial t}+\nabla\cdot\left(\mathbf{U}\langle\xi^k\rangle\right)-\nabla\cdot\left(\Gamma_T\nabla\langle\xi^k\rangle\right)=\frac{k\varepsilon_\xi}{\langle\xi'^2\rangle}\left(\langle\xi^{k-1}\rangle\langle\xi\rangle-\langle\xi^k\rangle\right)$$

Scale similarity

$$\frac{\varepsilon_\xi}{\langle\xi'^2\rangle}=C_\xi\frac{\varepsilon}{k}$$

Conditional moments of PBE

$$\frac{\partial\langle\underline{m}\rangle}{\partial t}+\nabla\cdot\left(\mathbf{U}\langle\underline{m}\rangle\right)-\nabla\cdot\left(\Gamma_T\nabla\langle\underline{m}\rangle\right)=\langle\underline{R}(\xi,\underline{m})\rangle$$

$$\frac{\partial\langle\xi\underline{m}\rangle}{\partial t}+\nabla\cdot\left(\mathbf{U}\langle\xi\underline{m}\rangle\right)-\nabla\cdot\left(\Gamma_T\nabla\langle\xi\underline{m}\rangle\right)=\frac{\varepsilon_\xi}{\langle\xi'^2\rangle}\left(\langle\xi\rangle\langle\underline{m}\rangle-\langle\xi\underline{m}\rangle\right)+\langle\xi\underline{R}(\xi,\underline{m})\rangle$$

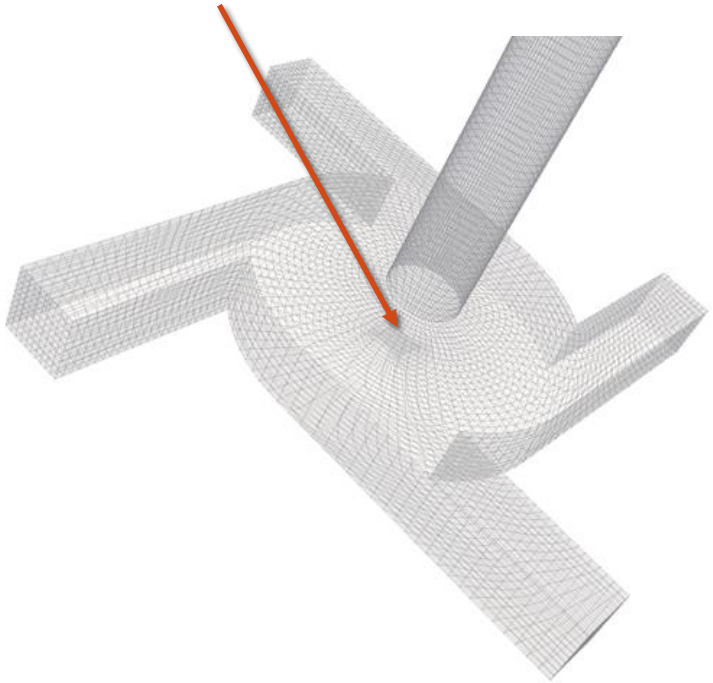
Source term for conditional PBE moments

$$\langle\underline{R}(\xi,\underline{m})\rangle=\sum_{\alpha=1}^{2}p_\alpha\underline{R}(\xi_\alpha,\underline{m}_\alpha)$$

$$\langle\underline{R}(\xi,\underline{m})\rangle=\sum_{\alpha=1}^{2}p_\alpha\xi_\alpha\underline{R}(\xi_\alpha,\underline{m}_\alpha)$$

PBE for FNP in MIVR – Predicted particle size

Particle size measured at the center of the mixing chamber



Mean particle size at the center of the mixing chamber

- Predicted by DQMOM (Cheng et al.,)
  - 4.37 of initial polymer length
- Predicted in present work
  - 4.01 of initial polymer length

Satisfactory agreement between the two models

Summary

A new conditional quadrature method of moments was developed for turbulent reactive mixing problems

The method avoids problems with singularity in the DQMOM formulation and preserves a larger number of moments than DQMOM

CQMOM has shown its efficiency controlling more moments than DQMOM at comparable computational cost

The PBE with aggregation kernel predicts the average size of particles formed in the MIVR in agreement with DQMOM

Thank you!