U.S. DEPARTMENT OF ENERGY

Nuclear Energy

NEAMS

NUCLEAR ENERGY ADVANCED MODELING & SIMULATION PROGRAM

Droplet Dynamics Modeling and Simulation for Aqueous Separation Application

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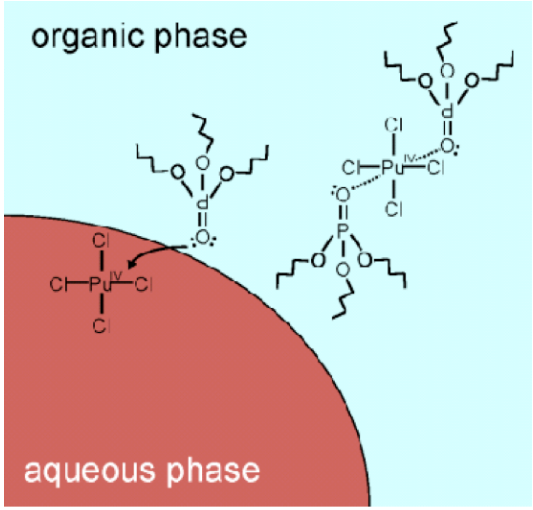
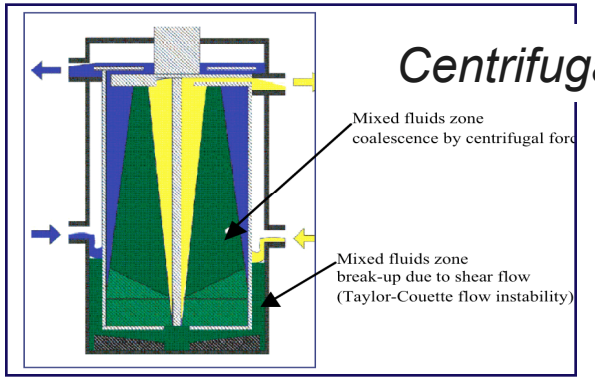
Understanding droplet dynamics is central to liquid-liquid extraction

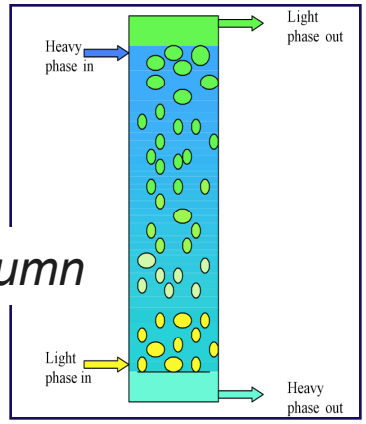
- Extraction takes place at liquid-liquid interface
- Liquid-liquid extraction devices
  - Pulsed column, centrifugal contactor, mixer settlers
  - Mixing of immiscible phases (organic/aqueous)
  - Generate large interfacial area
- Multiple droplets interaction with mass transfer
  - Interface dynamics: break-up, coalescence
  - Surfactant and Marangoni effects





Centrifugal contactor

Pulsed column



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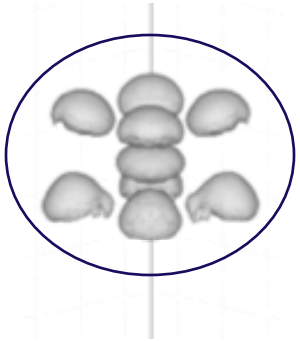
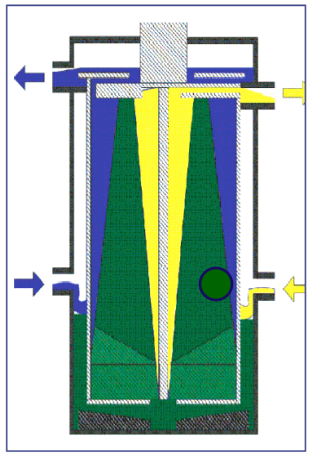
Multi-Scale Fluid Dynamics Simulation in Contactor



Flow regime information

Closure models

(drag, mass transfer coefficients)



At the droplet scale:

- Direct numerical simulation of fluid dynamics with chemical species diffusion-reaction and interface tracking method
- Requires high-resolution, about 20 grid points per droplet diameter, even more points for high Schmidt number

At the device scale:

- Reactive multiphase flow simulation
- Averaged formulation (Eulerian-Eulerian approach) with sub-grid scale models such as interfacial areas and interphase mass transfer

Path Towards High-Fidelity Simulation of Droplet Dynamics for Liquid-Liquid Extraction Processes

- **Goal: Develop computational capabilities to model and simulate with high-fidelity droplet dynamics with chemical diffusion-reaction including soluto-capillary effect in order to develop subscale model for drag and mass transfer**
- **Requires**
  - Development of mathematical formulation
  - Implementation of accurate numerical methods
  - Verification and validation
- **FY10 focus has been on the modeling of**
  - Discontinuity in species concentration at the interface
  - Soluto-capillary effect
  - Multiple species
  - Simple chemical reaction

Problem Formulation

- **Assumptions of current work**
  - Two immiscible Newtonian fluids
  - Incompressible flow
  - Isothermal

- **Governing equations**
  - Flow equations (mass and momentum conservation equations)

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \left(\rho \vec{u}\right) = 0$$

Surface tension

$$\frac{\partial \rho \vec{u}}{\partial t} + \nabla \cdot \left(\rho \vec{u}\vec{u}\right) = -\nabla P + \rho \vec{g} + \nabla \cdot \left(\mu\left(\nabla \vec{u} + \nabla^T \vec{u}\right)\right) + \sigma \kappa \delta \hat{n} + \nabla_S \sigma \delta$$

  - Species transport equation

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot \left(C_i \vec{u}\right) + \nabla \cdot \left(D_i \left(\nabla C_i\right)\right) + \sum_{j=1,m} r_{ij}$$

Interfacial Boundary Conditions

At a fluid-fluid interface with no phase change

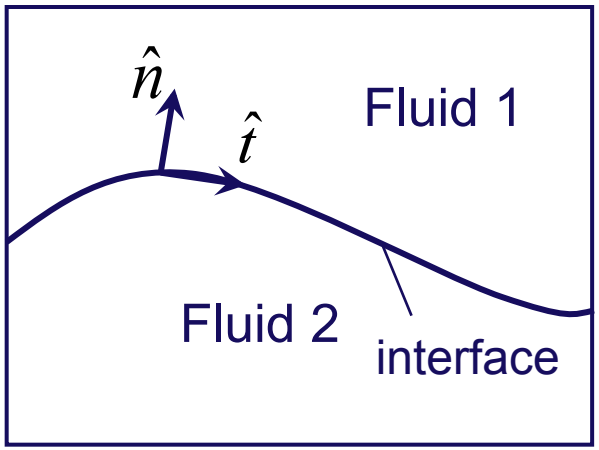
- Continuity Condition $\vec{V}_I = \vec{u}_1 = \vec{u}_2$
- Normal Stress Balance

$$P_2 - P_1 = \sigma\kappa + 2\mu_2 \hat{n}_k \left(\frac{\partial u_k}{\partial n}\right)_2 - 2\mu_1 \hat{n}_k \left(\frac{\partial u_k}{\partial n}\right)_1$$

- Tangential Stress Balance

$$\frac{\partial \sigma}{\partial s} = \mu_2 \left(\hat{t}_i \frac{\partial u_i}{\partial n} + \hat{n}_k \frac{\partial u_k}{\partial s}\right)_2 - \mu_1 \left(\hat{t}_i \frac{\partial u_i}{\partial n} + \hat{n}_k \frac{\partial u_k}{\partial s}\right)_1$$

σ surface tension coefficient, κ curvature



Surface tension coefficient varies with species concentration

$$D_{A1} \frac{\partial C_{A1}}{\partial n} = D_{A2} \frac{\partial C_{A2}}{\partial n}$$

$$\frac{C_{A2}}{C_{A1}} = m$$

At thermodynamic equilibrium

$$\sigma = \sigma_0 + \gamma\left(C_i - C_{ref}\right)$$

Global embedded interface formulation to model discontinuity in species concentration at interface

- **Reformulate the problem as an equivalent problem**

$$\frac{\partial a\psi}{\partial t} + \nabla \cdot \left(a\psi \vec{u} \right) = \nabla \cdot \left(aD\left(\nabla \psi \right) \right) \qquad a(x,t) = \begin{cases} 1, & x \text{ in } R_1 \\ m, & x \text{ in } R_2 \end{cases}$$

$$C_i = a\psi\big|_{R_i}, \quad i = 1,2 \qquad m > 0$$

- **Advantage:**
  - Global model with embedded interface condition treatment
  - No need to locally modify diffusion flux at the interface (as done in previous work in literature)

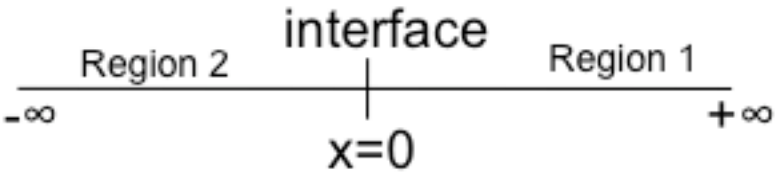
Numerical methods for the fluid flow

- **Incompressible flow solver**
  - Pressure correction projection method
  - Requires solving a Poisson equation with variable coefficient (density)
  - Finite-volume discretization
- **Interface tracking by volume tracking** (Rider and Kothe 1998)
  - Interface represented by amount of material fluids present in cell (volume fraction)
  - Interface is evolved by solving advection equation for volume fraction
  - Interface is reconstructed by piecewise linear planes to estimate accurate fluxes (avoid numerical diffusion)
  - Momentum fluxes consistent with geometrical mass fluxes enable us to do large density ratio
- **Balanced-force algorithm for surface tension** (Francois et al. 2006)
  - Balanced-force treatment of normal and tangential surface tension terms
  - Surface force method: continuum (CSF) and sharp (GFM) approach
  - Estimation of interface curvature: convolution and height function methods

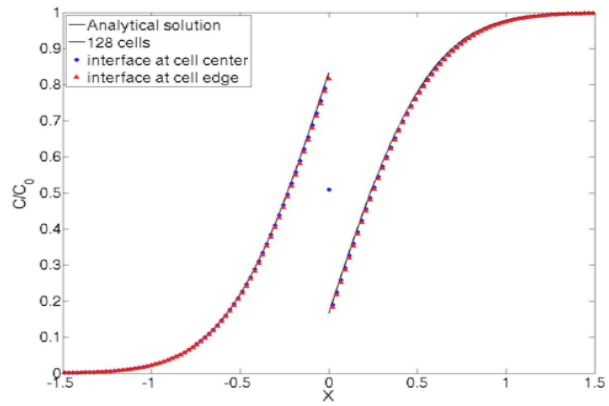
Numerical methods for species transport

- **Operator split in time: advection & diffusion**
  - Flow volume tracker computes species advection
  - Advected species appear as *given* sources in the diffusion system
- **Spatial discretization for the diffusion system**
  - Mimetic finite-difference method based on discrete analog of integral identity (Morel et al. 2001)
  - Accurate for unstructured meshes
  - Cell-averaged concentrations and net fluxes through faces
  - Locally conservative; more accurate diffusive fluxes
- **Time discretization for the diffusion system**
  - Fully-coupled, 1st and 2nd-order implicit time stepping (BDF1 and BDF2)
  - Nonlinear solver uses the nonlinear-Krylov accelerated inexact Newton method (Carlson and Miller 1998)
  - Decoupled, physics-based preconditioning using AMG (LLNL's Hypre package)
  - Error-based adaptive time step selection for BDF2 stepping.

Verification of Global Embedded Interface Model
1D Diffusion with Species Discontinuity at the Interface

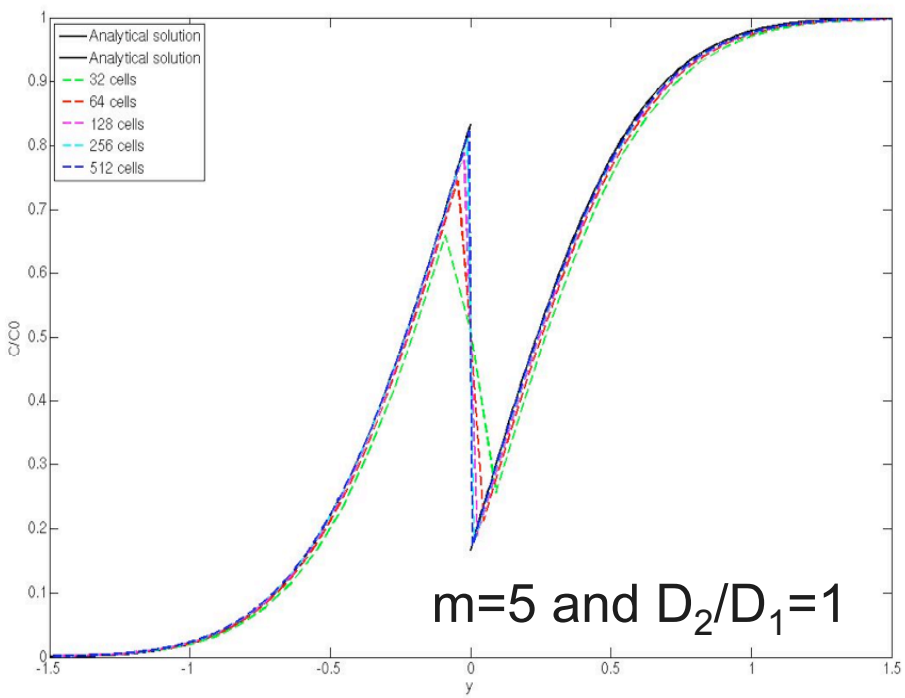


$$\frac{C_2}{C_0} = \frac{m}{1+m\sqrt{D_2/D_1}}\, erfc\left(\frac{|x|}{2\sqrt{D_2 t}}\right) \qquad \frac{C_1}{C_0} = \frac{1}{1+m\sqrt{D_2/D_1}}\left\{1+m\sqrt{D_2/D_1}\, erf\left(\frac{x}{2\sqrt{D_1 t}}\right)\right\}$$

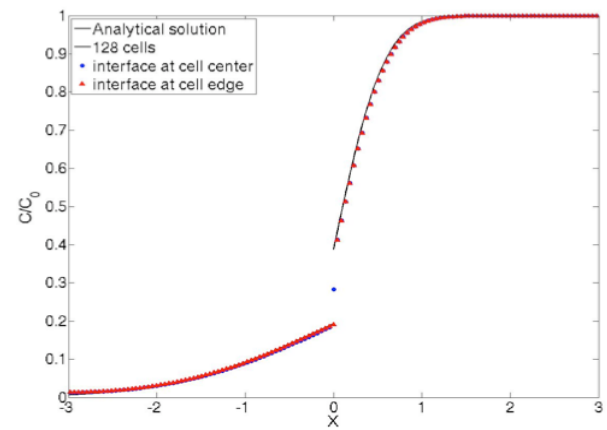


m=5 and D_2/D_1=1

Mesh Resolution Effects



m=5 and D_2/D_1=1



m=0.5 and D_2/D_1=10

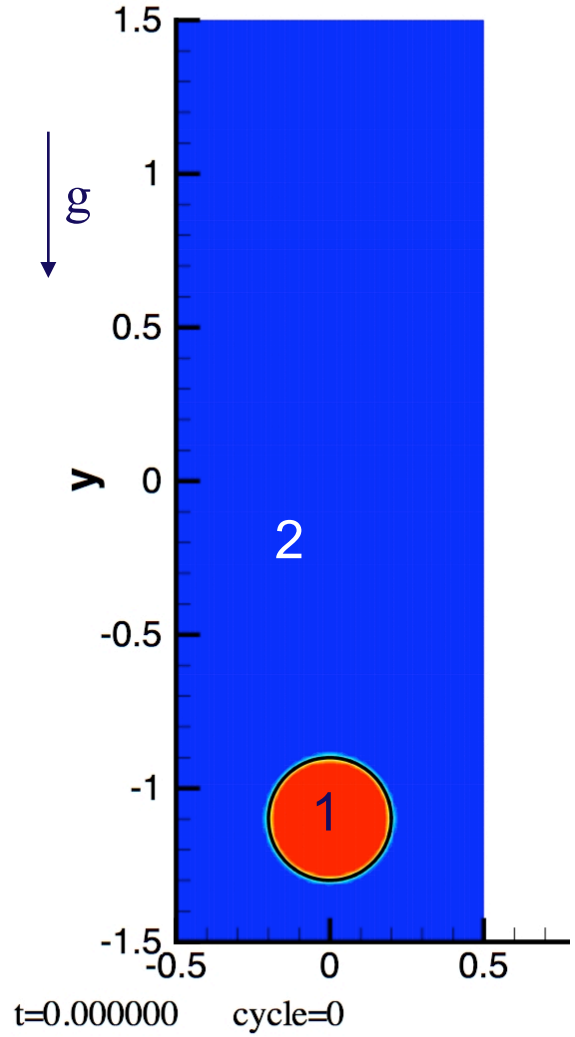
Simulation of Rising Droplet by Buoyancy Capability demonstration

- 2D and 3D single droplet rising by buoyancy
- Single species diffusion and advection
- Soluto-capillary effect and simple reaction
- Reference velocity $U = \sqrt{gd}$
- Non-dimensional parameters

$$\mathrm{Re}_1 = \frac{\rho_1 U d}{\mu_1} \qquad \mathrm{Re}_2 = \frac{\rho_2 U d}{\mu_2}$$ *Reynolds number*

$$We_1 = \frac{\rho_1 U^2 d}{\sigma} \qquad We_2 = \frac{\rho_2 U^2 d}{\sigma}$$ *Weber number*

$$Pe_1 = \frac{U d}{D_1} \qquad Pe_2 = \frac{U d}{D_2}$$ *Peclet number*



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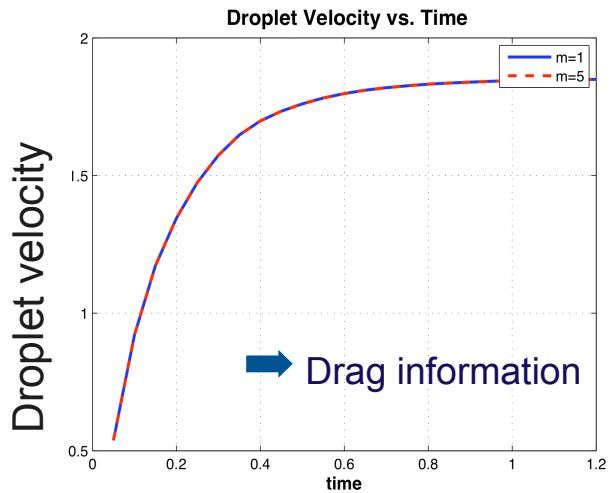
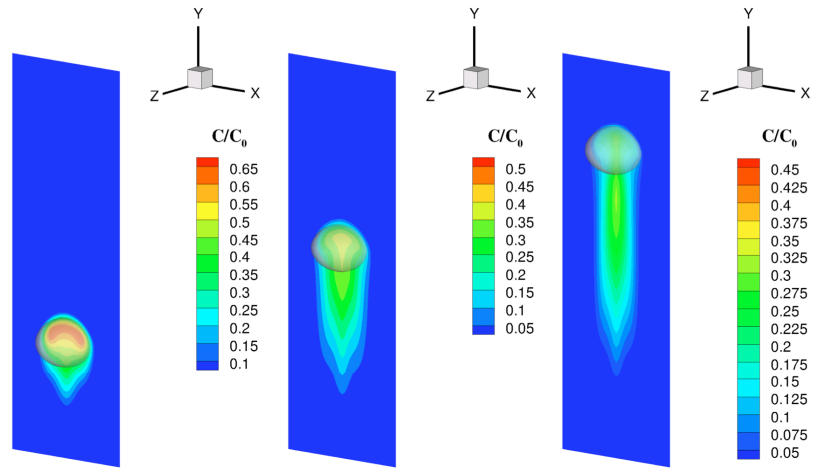
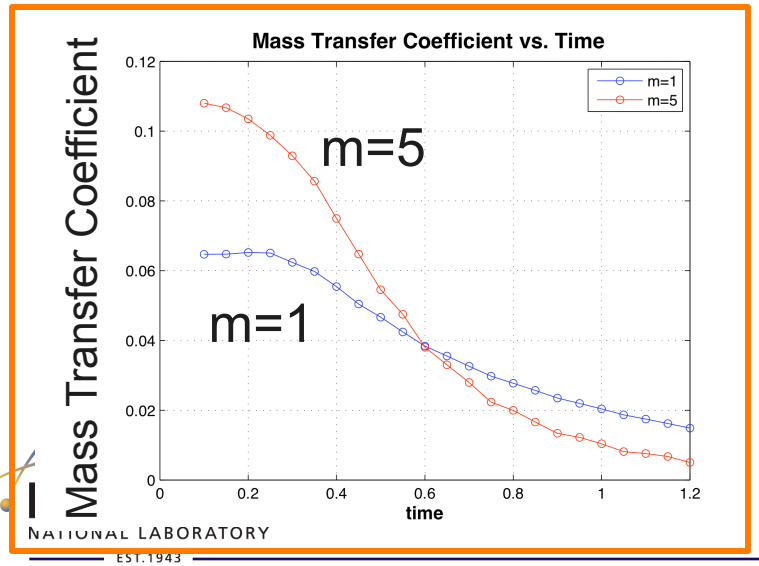
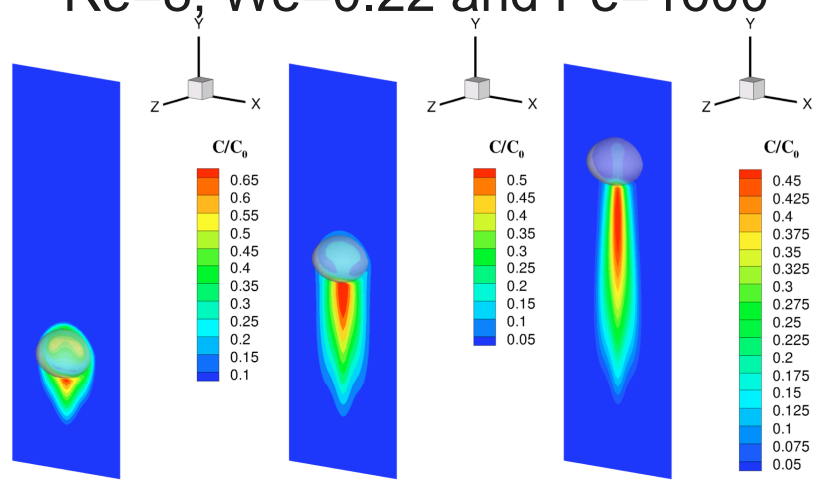
3D Simulation - Effect of distribution coefficient
Constant surface tension coefficient





Re=8, We=0.22 and Pe=1600





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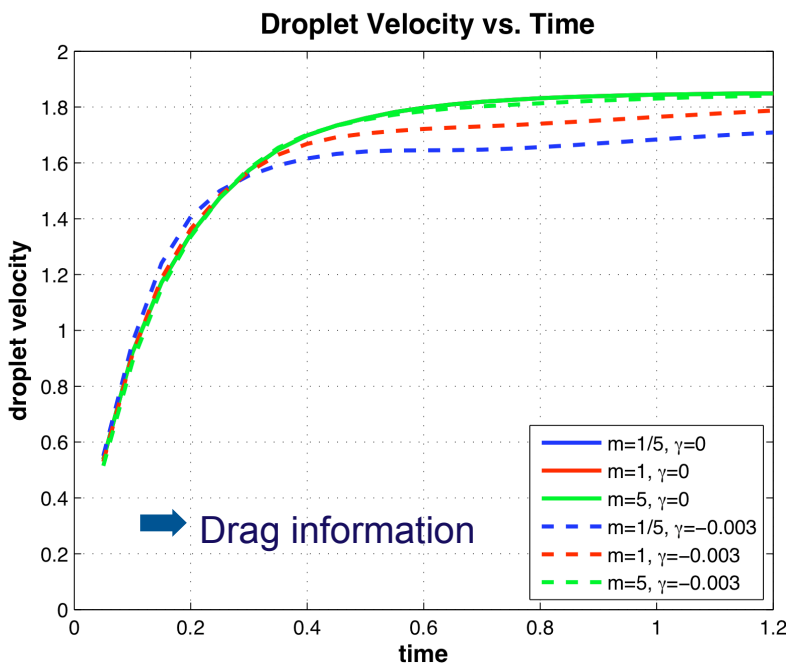
3D Droplet Rising by Buoyancy
Soluto-capillary effect affects droplet velocity
Distribution coefficient affects mass transfer coefficient

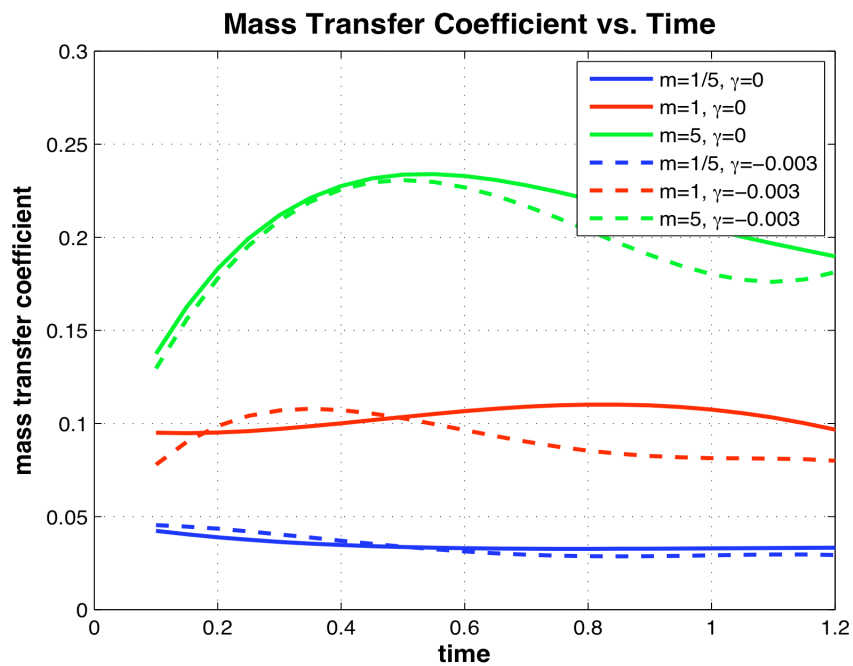
- Droplet velocity and concentration
- Mass transfer coefficient

$$\overline{V} = \frac{\sum V_y \cdot f_1}{\sum f_1} \qquad \overline{C} = \frac{\sum C \cdot f_1}{\sum f_1}$$

$$k(t) = \frac{V_d}{A_d \Delta t} \frac{\left(\overline{C}^{n+1} - \overline{C}^{n}\right)}{\overline{C}^{n}}$$

V_d drop volume
A_d interface area



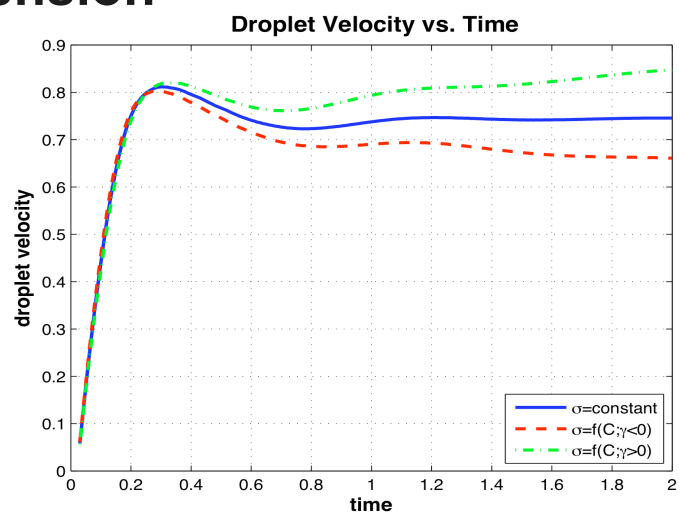


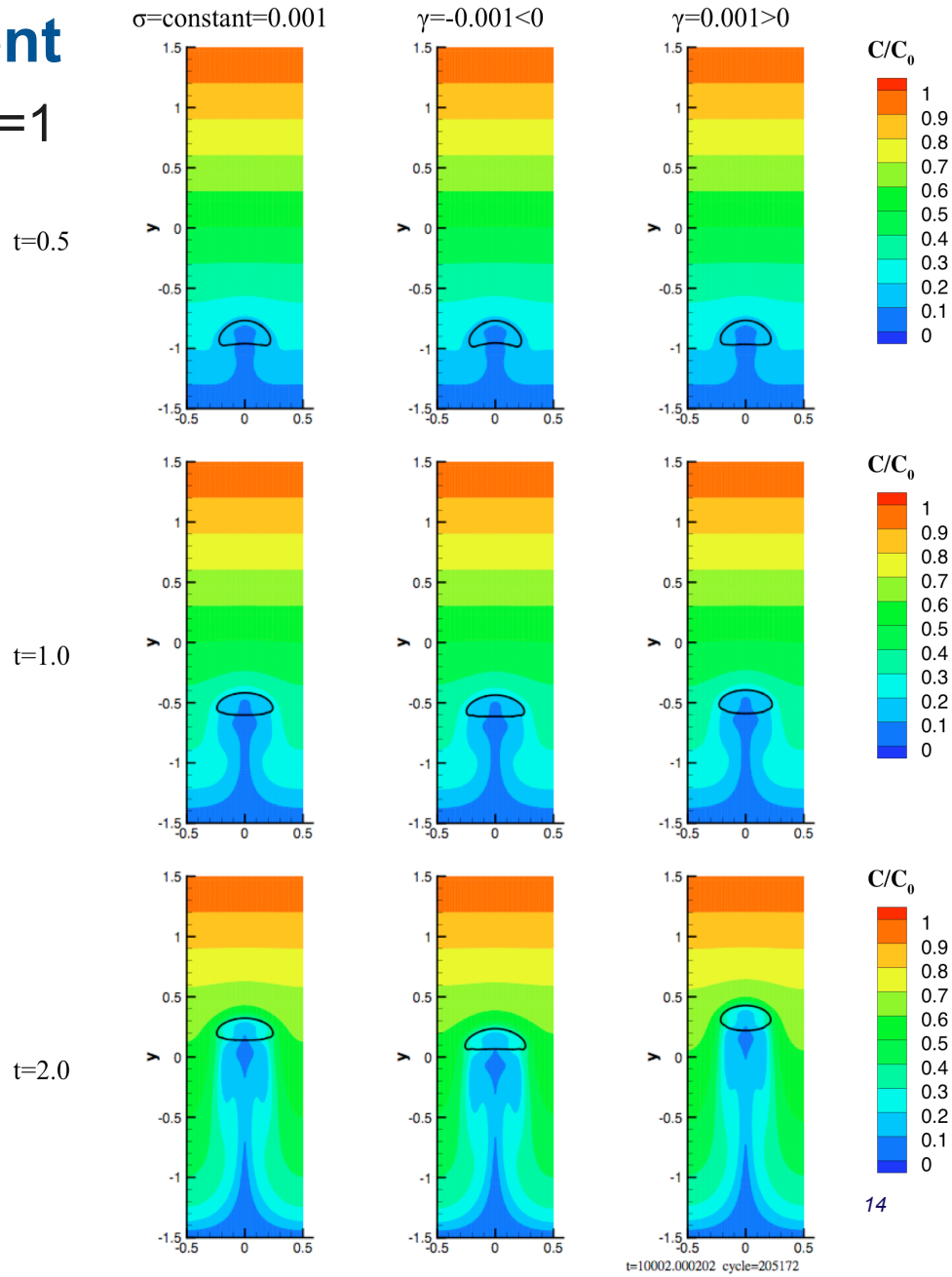
Re=8, We=0.22 and Pe=1600

Soluto-Capillary Effect Droplet initially in a gradient field (2D simulation)

m=1

- Species concentration gradient affects the fluid dynamics (two-way coupling)
- Different droplet shapes and velocity compared to case with constant surface tension





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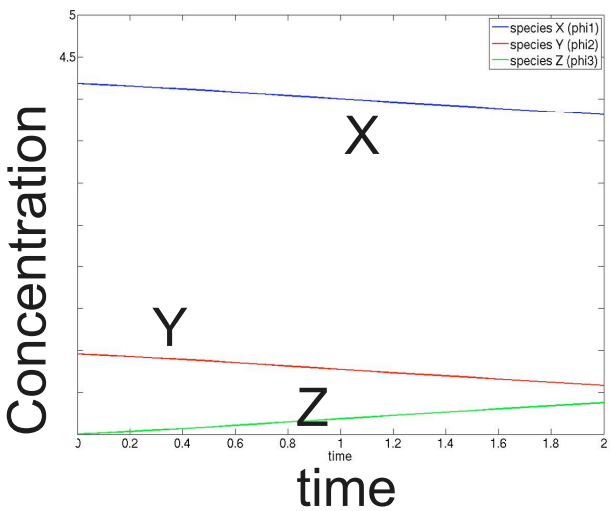
2D Simulation of a Simple Reaction X+Y→ Z Capability Demonstration

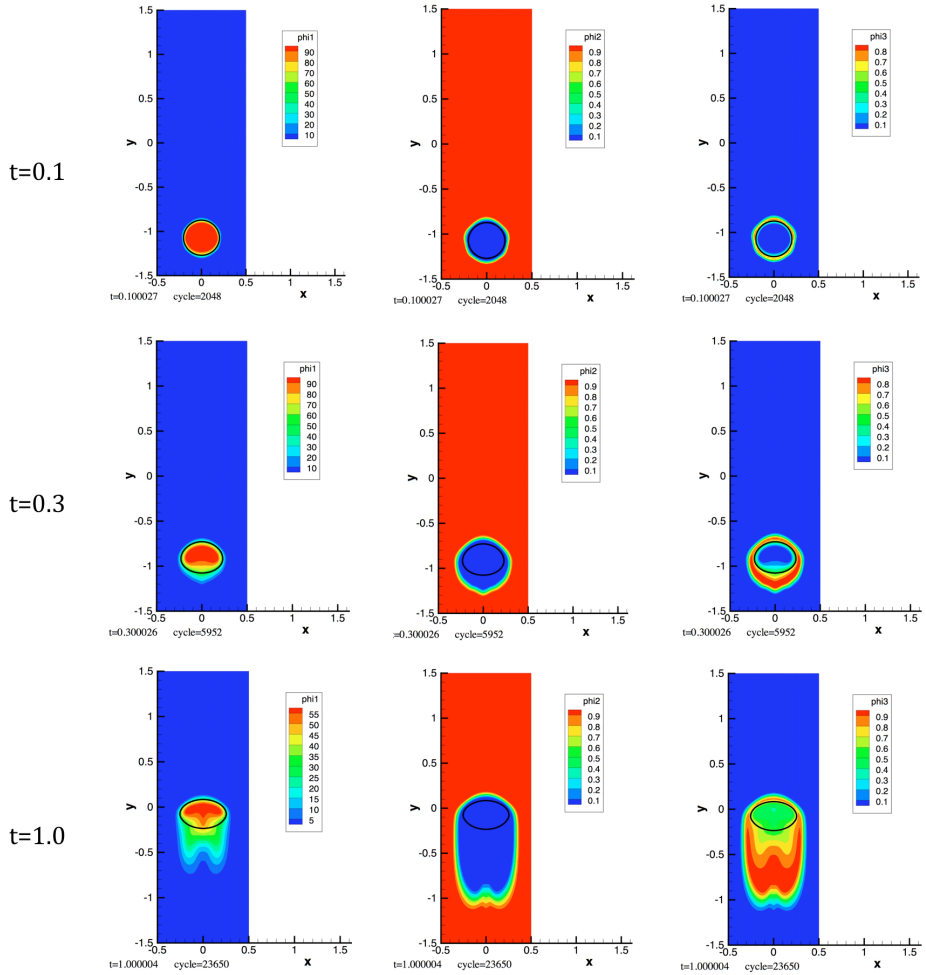
$$\frac{\partial C_X}{\partial t} = -\nabla\cdot\left(C_X\vec{u}\right) + \nabla\cdot\left(D_X\left(\nabla C_X\right)\right) - k_1 C_X C_Y$$

$$\frac{\partial C_Y}{\partial t} = -\nabla\cdot\left(C_Y\vec{u}\right) + \nabla\cdot\left(D_Y\left(\nabla C_Y\right)\right) - k_1 C_X C_Y$$

$$\frac{\partial C_Z}{\partial t} = -\nabla\cdot\left(C_Z\vec{u}\right) + \nabla\cdot\left(D_Z\left(\nabla C_Z\right)\right) + k_1 C_X C_Y$$

Re=8, We=0.22 and Pe=1600





Species X Species Y Species Z

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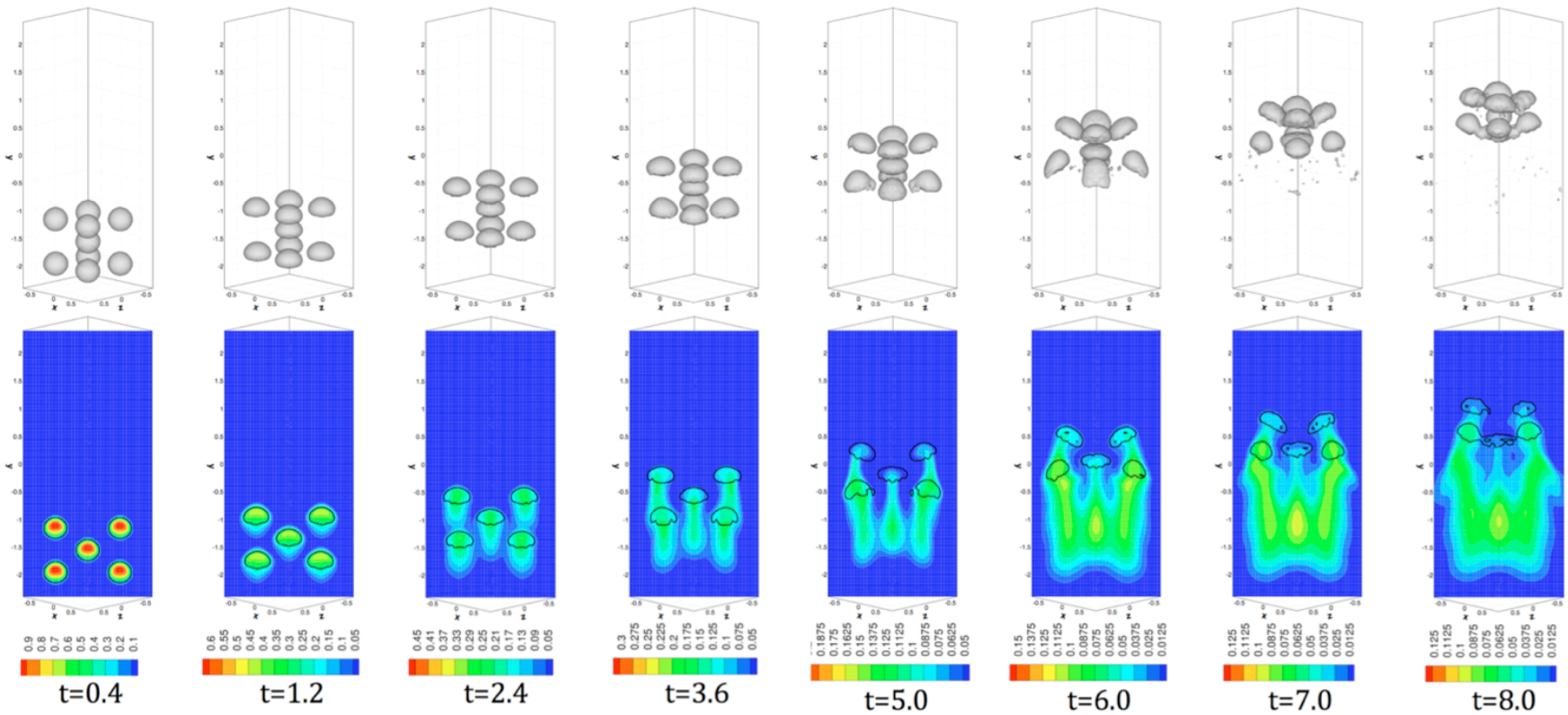
Multiple Droplet Dynamics – Preliminary Simulation

Re=100, We=0.036, Pe=100



Conclusions

- We have developed our computational capabilities towards high-fidelity simulation of droplet dynamics with mass transfer
- Our capability can model the discontinuity of species concentration at the interface and soluto-capillary effect
- Distribution coefficient affects the mass transfer coefficient. Larger distribution coefficient larger mass transfer coefficient.
- Soluto-capillary phenomenon affects the droplet dynamics (shape and velocity). Positive gradient less deformation and faster rise.
- We have also extended our capability to consider multiple species and simple reaction.

Challenging Issues and Future Work

- **Challenging numerical issues**
  - High Schmidt number requires a much finer mesh for accurate solution of the mass diffusion
  - Numerical stability of surface tension algorithm
- **In the future, we plan to**
  - perform validation with INL experiments
  - perform large scale simulation of multiple droplets
  - develop up-scaling theory to integrate the droplet level simulation to the device scale multiphase CFD simulation
  - model surfactant
  - study break-up and coalescence