SAND2012-10506P

Multiscale Models of Nuclear Waste Reprocessing: From the Mesoscale to the Plant-Scale

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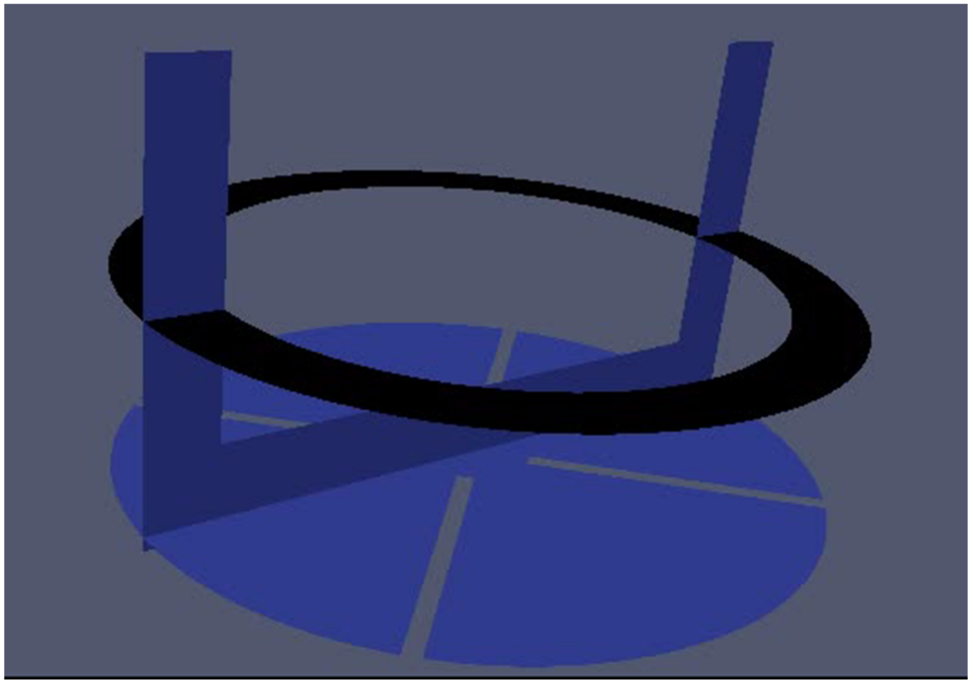

Turbulent (LES) single phase simulations of centrifugal contactor from Sierra Mechanics

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

NNSA National Nuclear Security Administration

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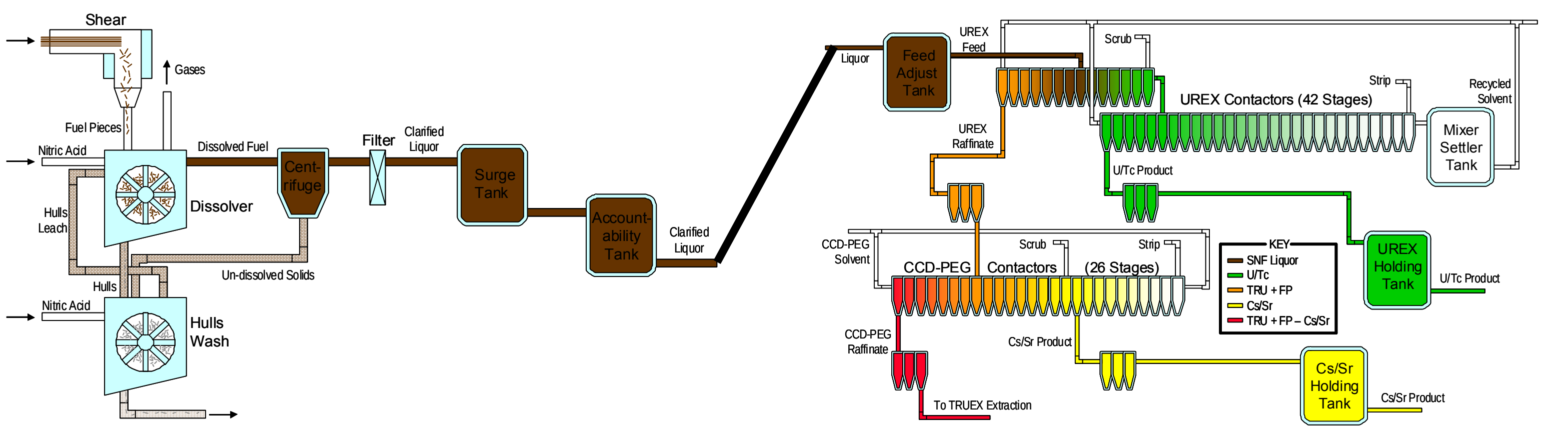
Project Vision: A Scientific Approach to Nuclear Waste Reprocessing

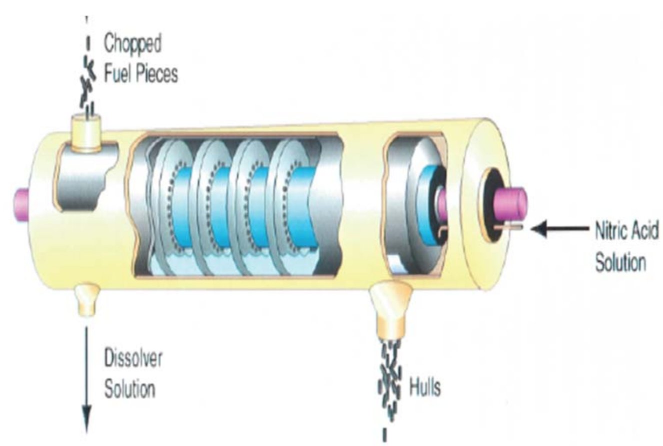
- The amount of nuclear waste produced and stored can be greatly reduced through reprocessing, where fuel rods are separated into various streams, some of which can be reused in reactors
- Current process developed in the 1950s and is dirty and expensive
  - U/Pu separation is the most critical => PUREX
- Our approach =>use science and simulation-based approach to develop a modern reprocessing plant
  - Leverage unique Sandia capability, SIERRA Mechanics, to model coupled physics via high performance computing
  - Models of reprocessing plants are needed to support nuclear materials accountancy, nonproliferation, plant design, and plant scale up



Secretary Energy Chu is very supportive of the “closed fuel cycle”

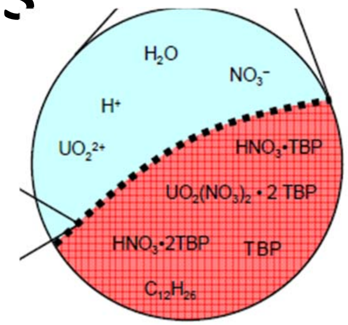
Detailed Model of PUREX-type Processes

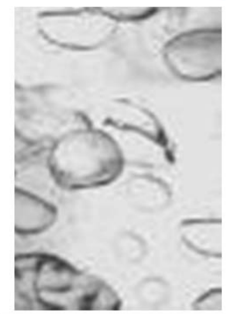
- Spent fuel rods are sheared and dissolved in acid
- Concentrated aqueous solution is then emulsified in a liquid-liquid extraction continuous contactor with a organic solvent continuous phase (TBP/dodecane)
- Uranium and plutonium oxide ions are then preferentially taken up by organic phase
- Centrifugal contactors used to enhance mixing and form aqueous droplets in organic continuous phase
- Maximize surface area for potential mass transport across the interface
- Up to five phases can occur simultaneously
- Criticality issues determine scale-up

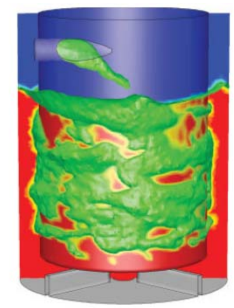


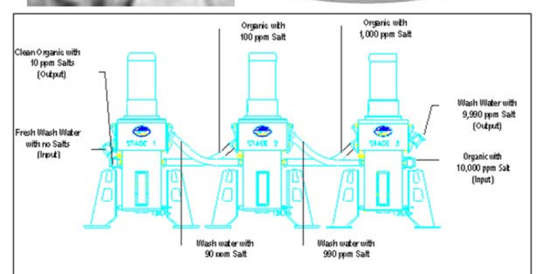
Missing Physics Models To Be Developed at Multiple Length Scales

- Droplet-scale model
  - **Interfacial mass transfer and fluid mechanics**
  - Surface variables, surfactants and Marangoni effects
  - Advection and diffusion in concentrated ionic, multiphase solutions
    - Stefan-Maxwell equation for mass flux
- Single-stage models
  - **Direct numerical simulation of multiphase, turbulent, immiscible flows with interfacial mass transport**
  - Integration of neutronics for criticality
  - Solid-fluid interactions models for complex rotors
- Unit-operations, column scale simulations
  - Optimization
  - Solvent evaluation, virtual radioactive experiments
  - **Reduced-order column model based on population balances**
- Integration with plant flow sheets models for nonproliferation
  - **High-fidelity plant model** for non-proliferation, process control, and accident mitigation
- Validation at all scales
  - **Droplet-scale experiments**
  - **Contactor-scale experiments**

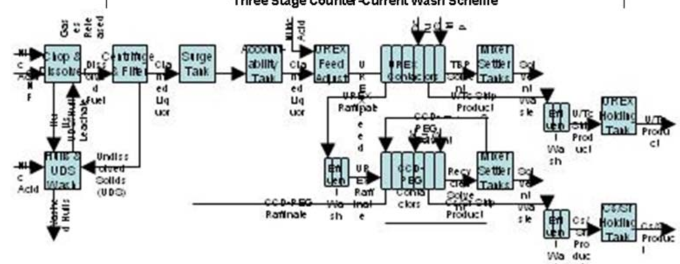




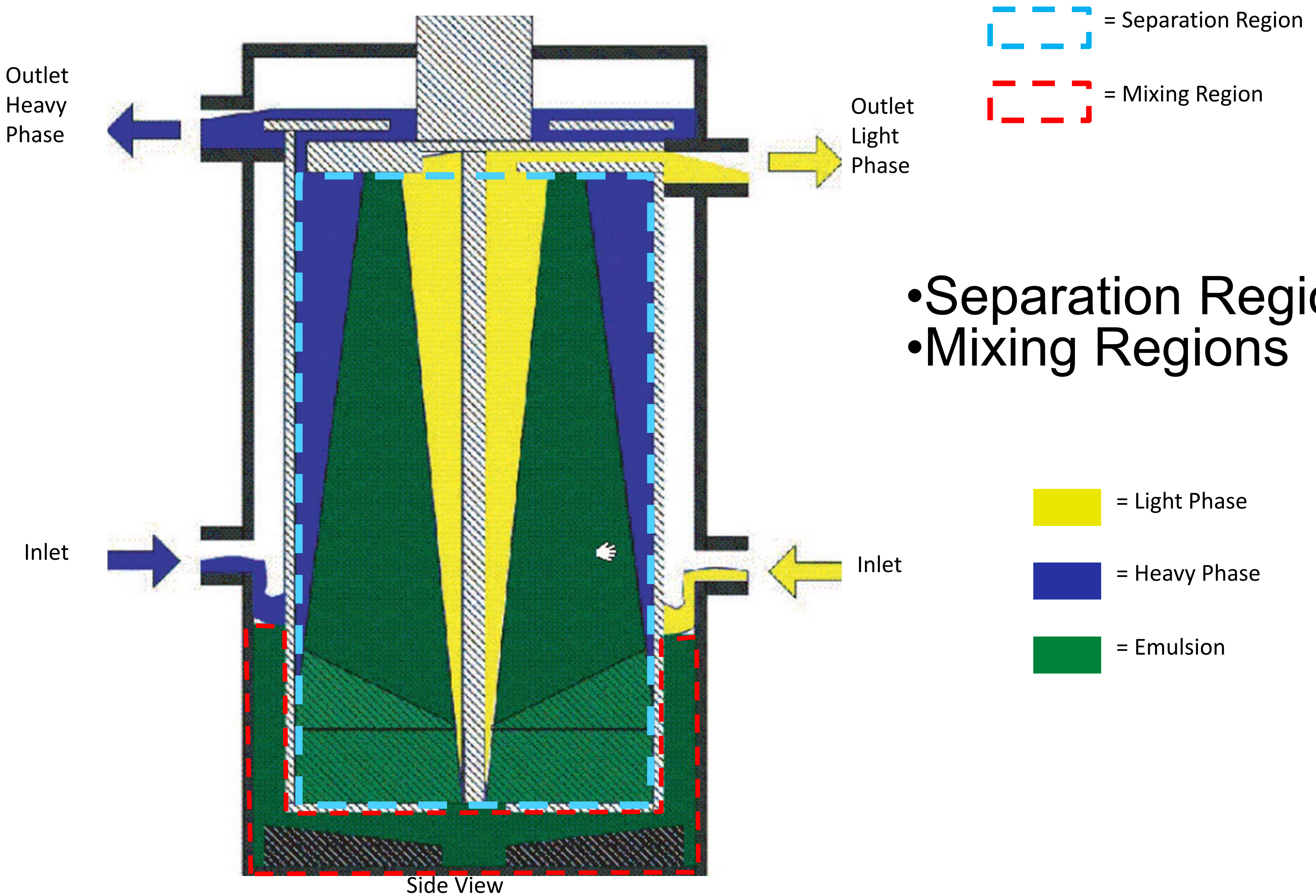




Three Stage Counter-Current Wash Scheme



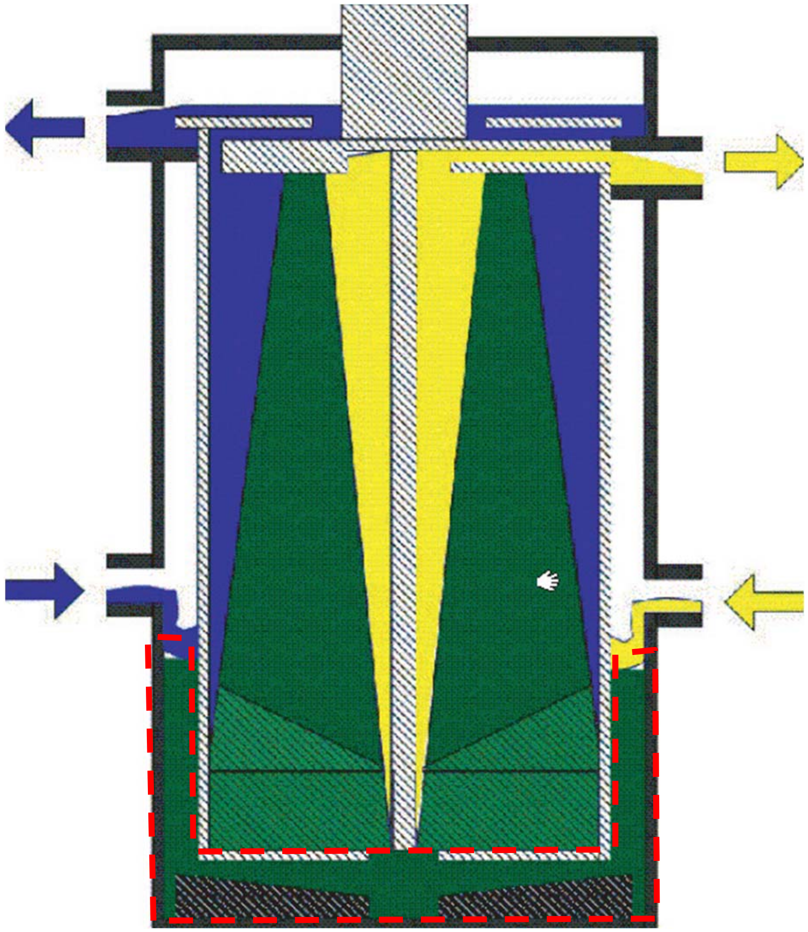
Annular Centrifugal Contactor

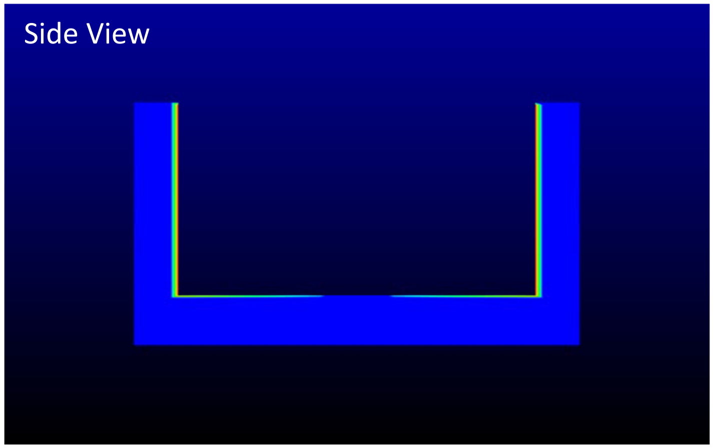


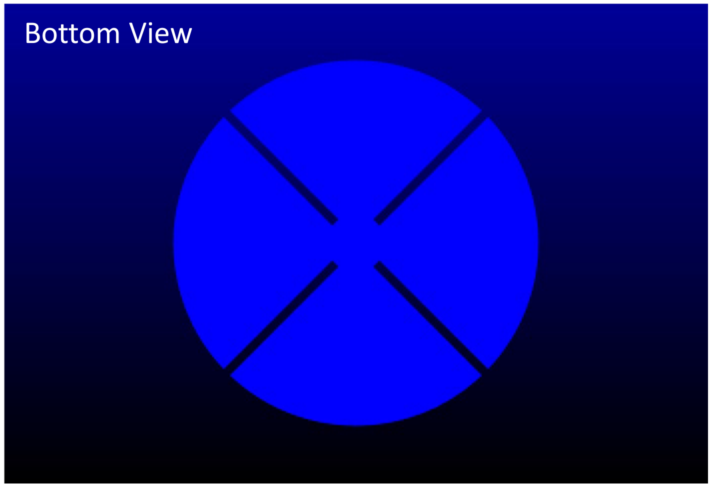
- Separation Regions
- Mixing Regions

Contactor – Mixing Region

ksgs Turbulence Model with a Single Phase

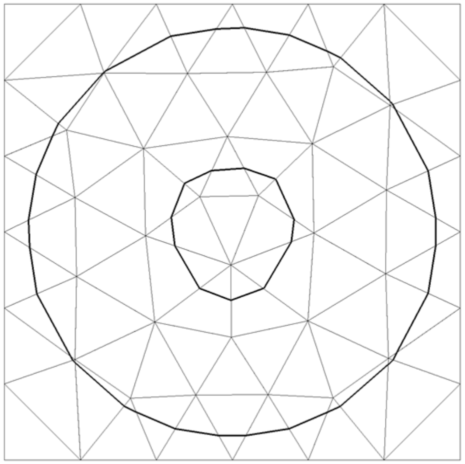


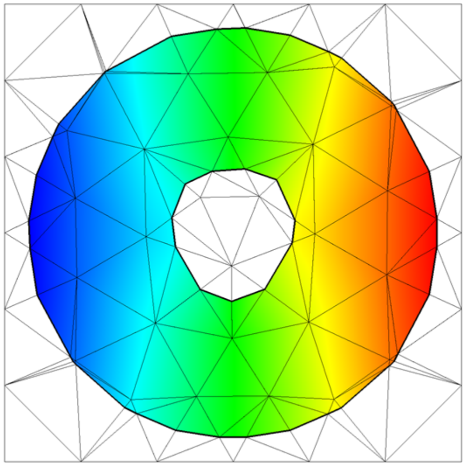




- Sierra/Aria transient turbulence model of contactor – largest production Aria calculation to date
- Currently working on two-phase models of contactor mixing zones
- Working on diffuse interface and CDFEM implementation

Droplet-Scale Methodology: Conformal Decomposition Finite Element Method





Simple Concept

- Use one or more level set fields to define materials or phases
- Decompose non-conformal elements into conformal ones
- Obtain solutions on conformal elements

Related Work

- Li et al. (2003) FEM on Cartesian Grid with Added Nodes
  - Focus on Cartesian Grid. Considered undesirable because it lost original mesh structure.
- Ilinca and Hetu (2010) Finite Element Immersed Boundary
  - Focus on solid-fluid with Dirichlet BCs

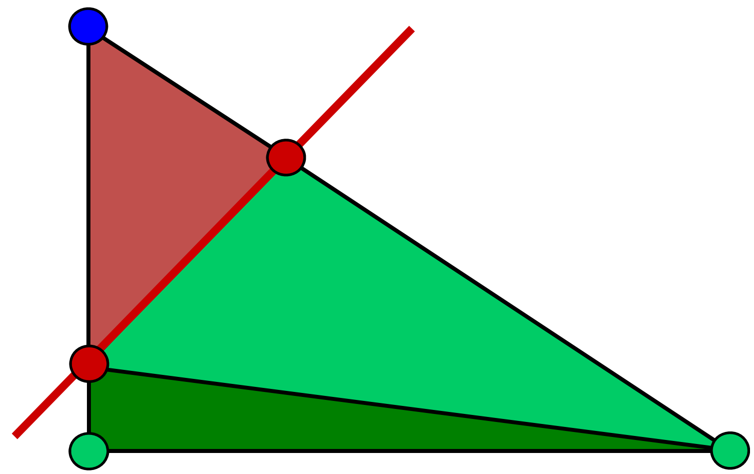
Properties

- Supports wide variety of interfacial conditions (identical to boundary fitted mesh)
- Avoids manual generation of boundary fitted mesh
- Supports general topological evolution (subject to mesh resolution)
- Similar to finite element adaptivity
- Uses standard finite element assembly including data structures, interpolation, quadrature

•CDFEM shown convergent for steady flow, Noble et al, IJNMF, 2010
•Extension to moving boundary problems

CDFEM – Constrained Spaces for Stability and Robustness

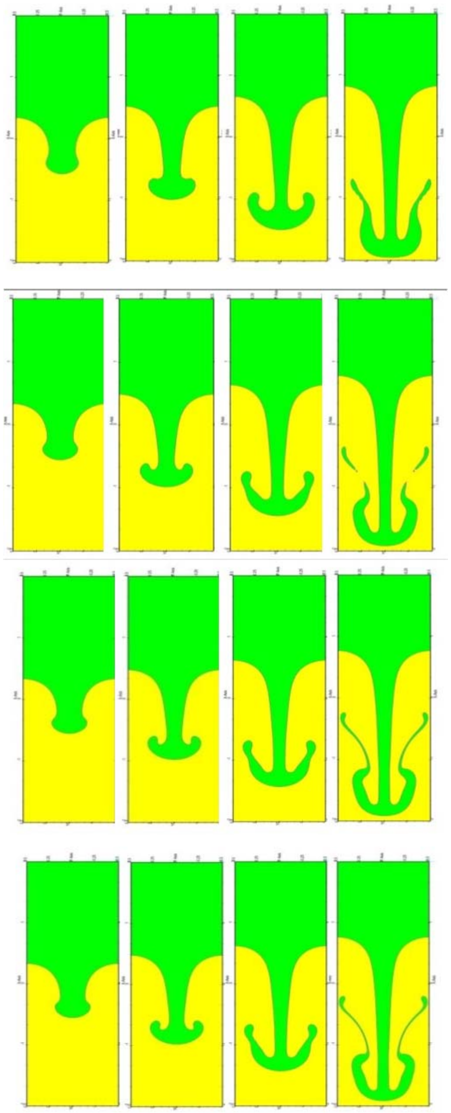
- Discrete Space Considerations in CDFEM
  - Anecdotal evidence for space requirements
    - Static, diffusive problems have shown optimal convergence rates using subelements
    - Dynamic, advection problems have shown poorly controlled modes in pressure-velocity and level set fields
  - Since interface is discretized as piecewise linear (PL) function on parent element, it follows that level set field should be constrained to be piecewise linear
  - A sufficient condition (but possibly overly strict) for a piecewise linear level set function is constraining velocity to be piecewise linear
  - Piecewise linear velocity suggests piecewise linear pressure
  - Constraints are imposed using linear system infrastructure used for hanging node constraints
  - Space used by Fries et al, 2010 for XFEM of two-phase and free surface flows since unconstrained space was unstable



Discrete spaces used in this work

- Level set is PL on parent element
- Velocity is PL on parent element
- Pressure is PL on parent element for each phase (separate PL field for each phase)

2D Rayleigh-Taylor Instability using CDFEM

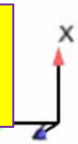


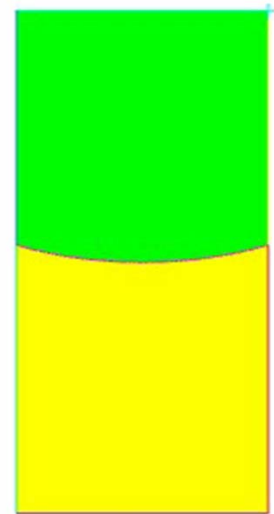
2.254% (1.95493)
h=1/20; Δt=h/3

1.014% (1.97972)
h=1/40; Δt=h/3.0

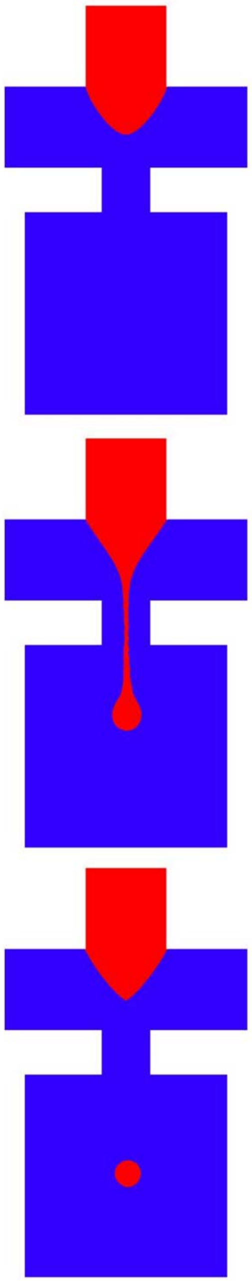
0.89% (1.9822)
h=1/80; Δt=h/3.0

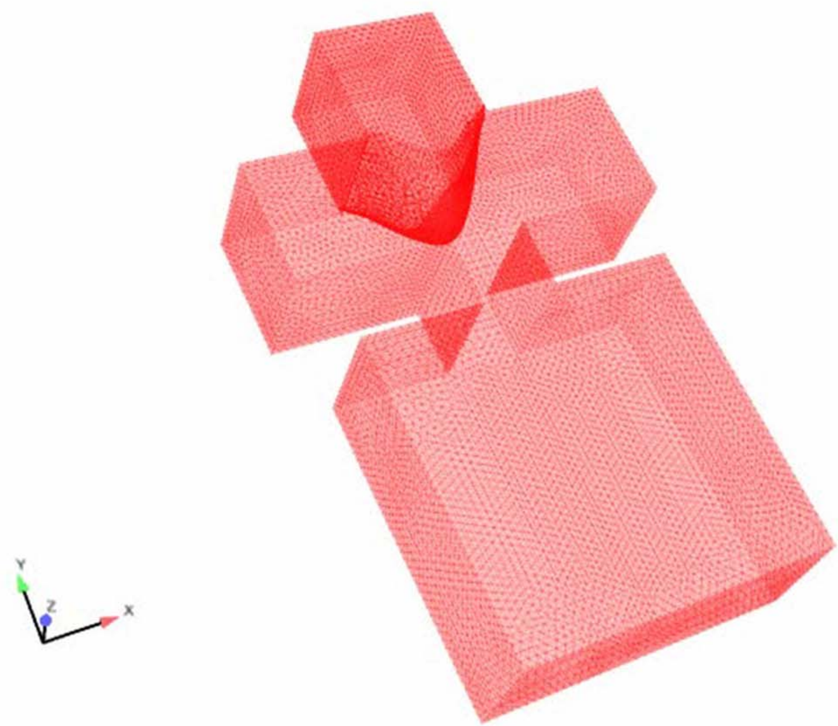
0.145% (1.9971)
h=1/160; Δt=h/3.0





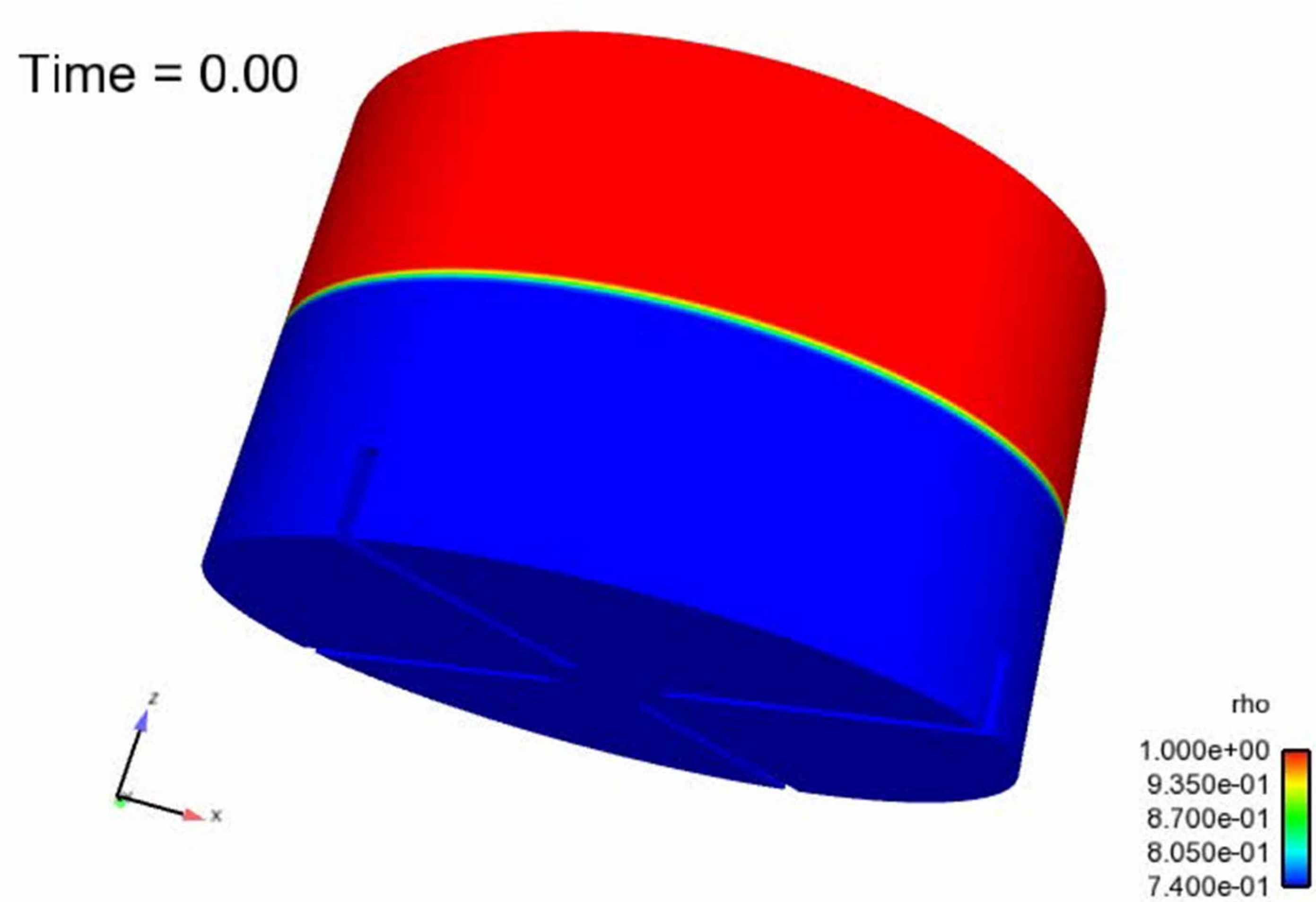
μFluid Flow Focusing Droplet Generator



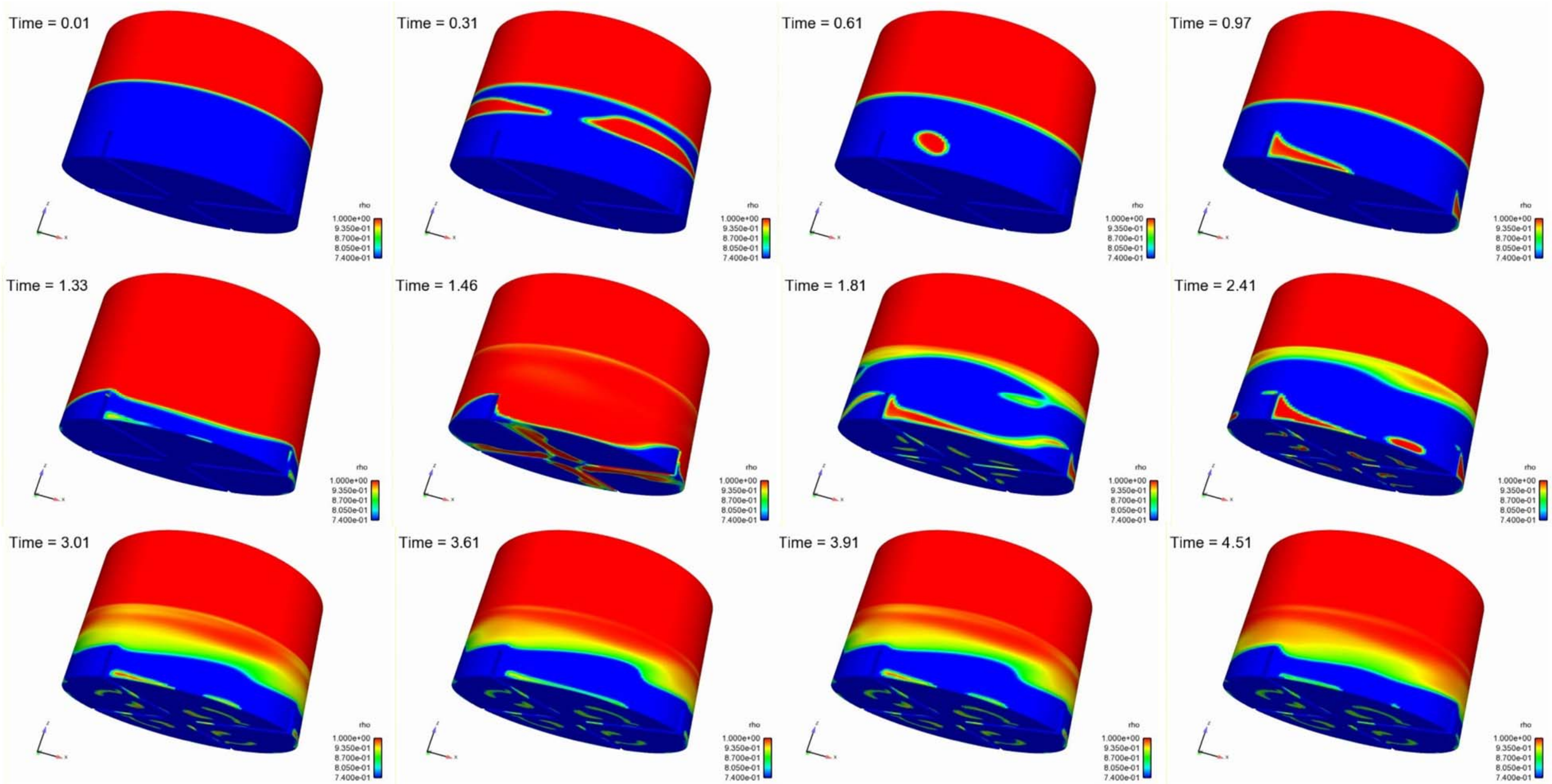


CDFEM method is able to transition from coflowing fluid to droplet generation regimes.

Mixing Two Fluids in a Centrifugal Contactor (CVFEM/Level Set)

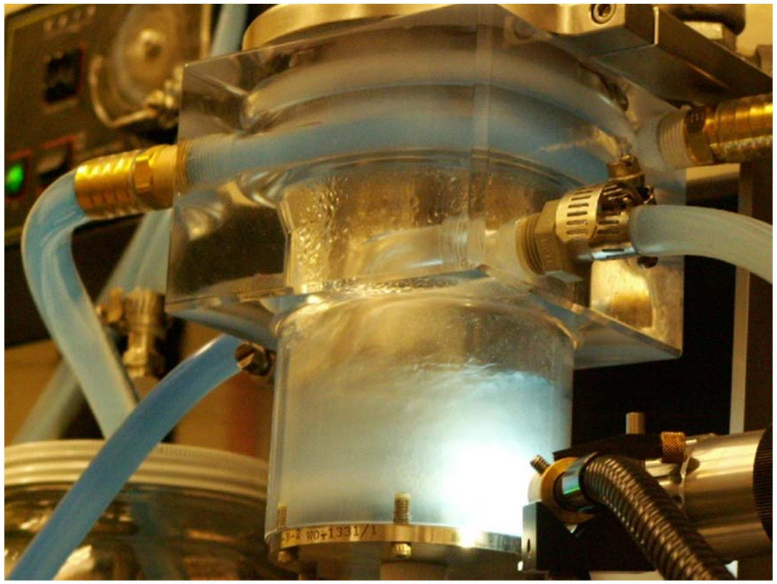


2phase Contactor: CVFEM/LS

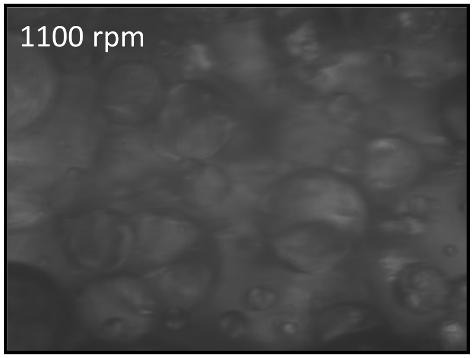


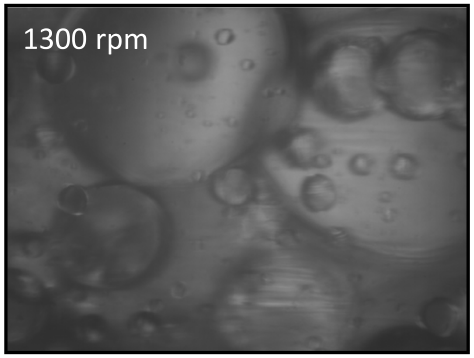
Centrifugal Contactor Experiments

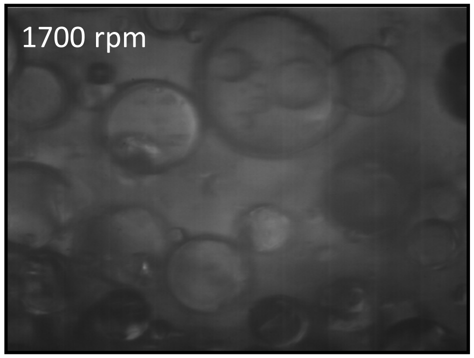
- Test Materials: PDMS and Water
- Rotor Speeds: 1100 – 2100 rpm
- Camera focused at inner surface of outer cylinder
- Camera is about 2 mm above bottom of rotor
- Total liquid height in gap is about ¾ - 1in
- Drop size detection limit – 30 µm



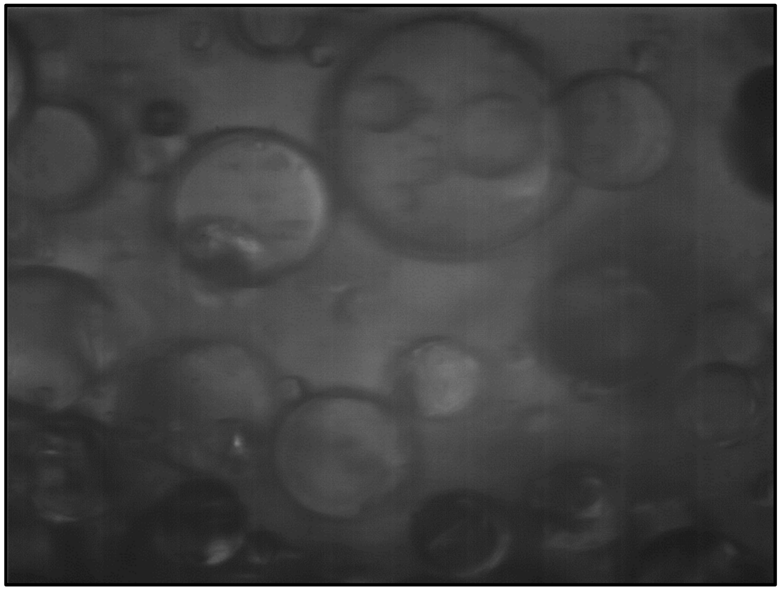
High Speed Camera



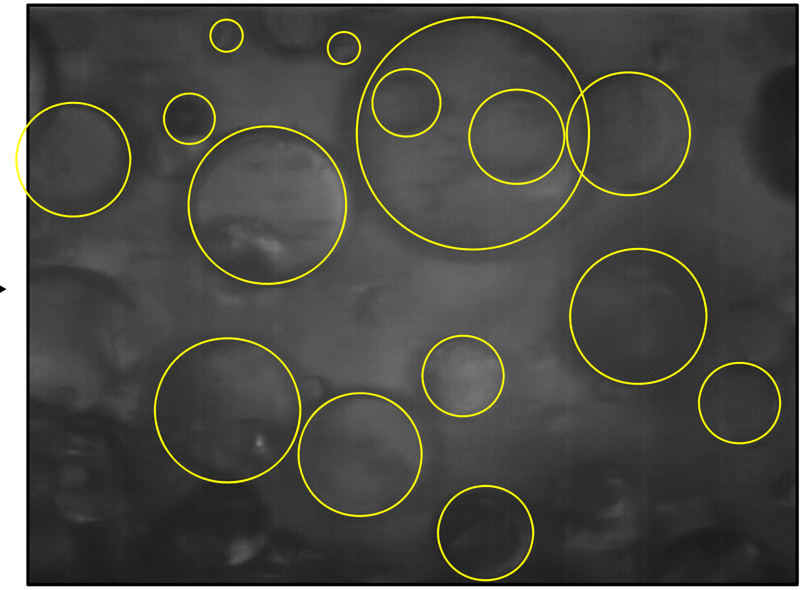




Drop Size Analysis

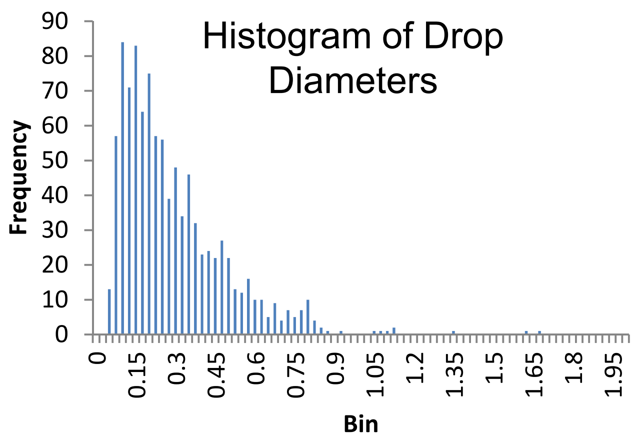


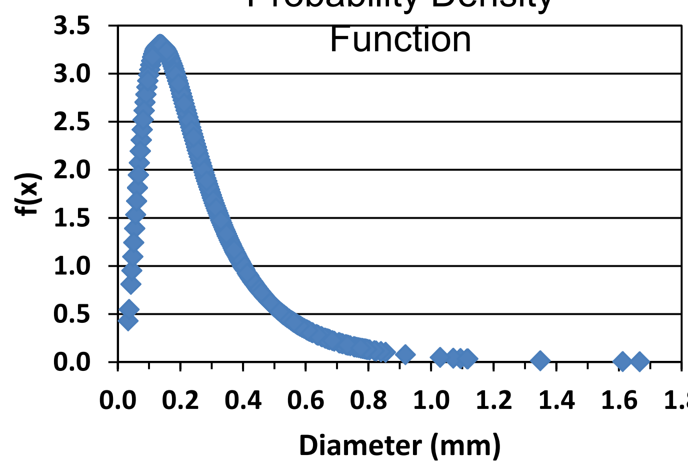
ImageJ



For brevity here, not all droplets were circled

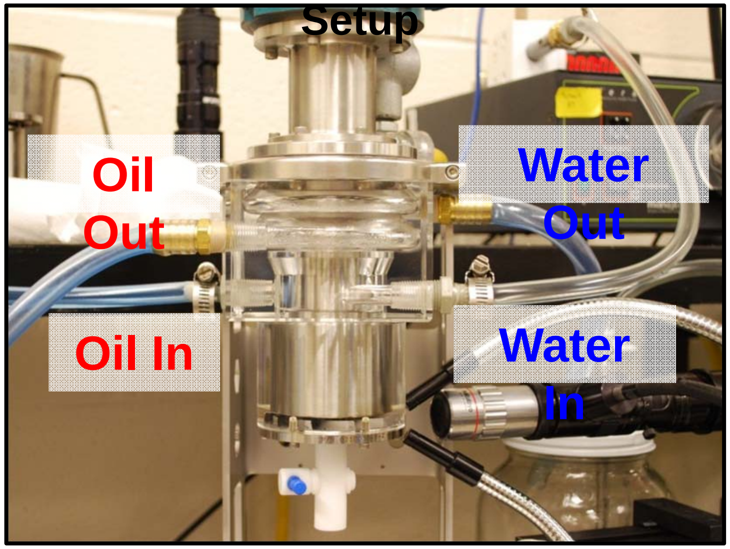
Based on a calibration image (209 pixels = 0.625mm), ImageJ calculates the diameter of each of the indicated (yellow) circles. These data are then transferred into Excel where probability densities of the distributions are calculated.



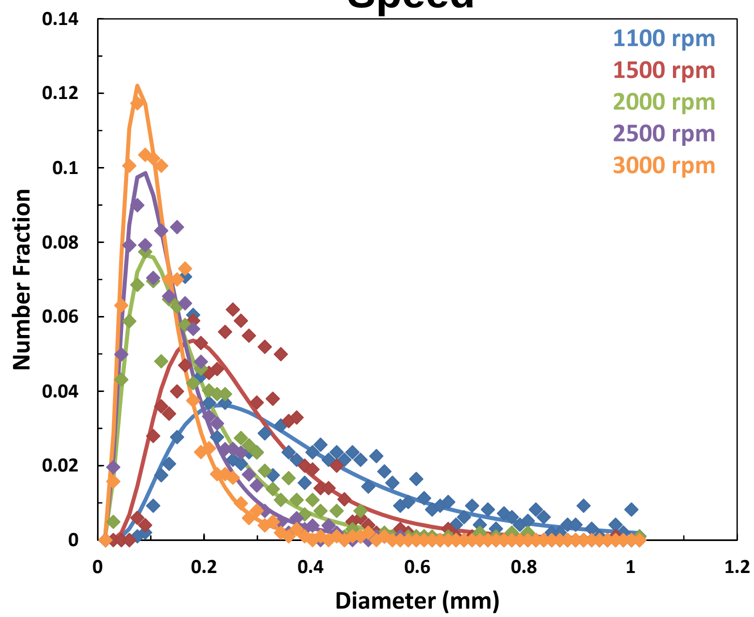


Drop Size Measurements in a Centrifugal Contactor

Centrifugal Contactor Experimental Setup

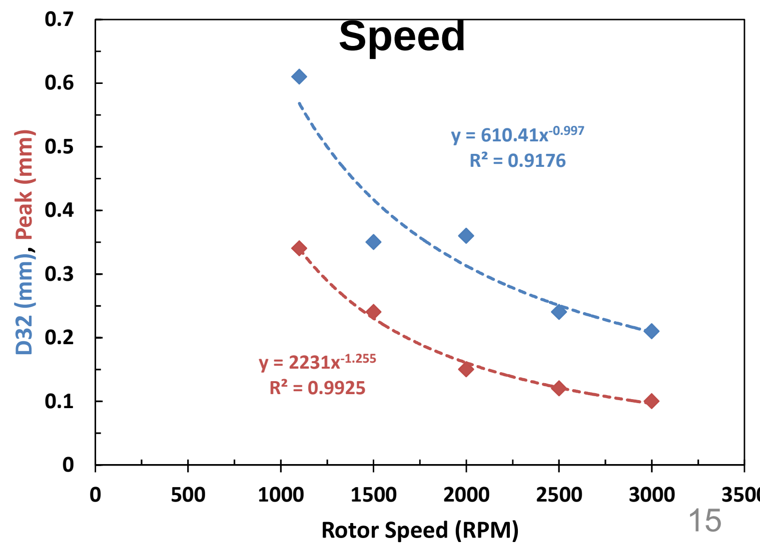


Drop Size Distributions with Rotor Speed



- Laser fluorescence is used to measure oil droplet size distributions in a turbulent, three-phase mixing system
- Drop size distributions are the result of an equilibrium state between drop breakup and coalescence
- Drop size distributions are lognormal for all rotor speeds tested
- Distributions narrow and shift to smaller sizes with increasing rotor speeds as the larger droplets break
- Mass transport experiment underway
- Average drop size and Sauter mean diameter show a power law dependence on rotor speed
- **Two presentations, collaboration with ANL, and AIChE paper underway**

Sauter Mean Diameter and Rotor Speed



Population Balance Model of Drop Size Distribution and Mass Transport

In mixing zone

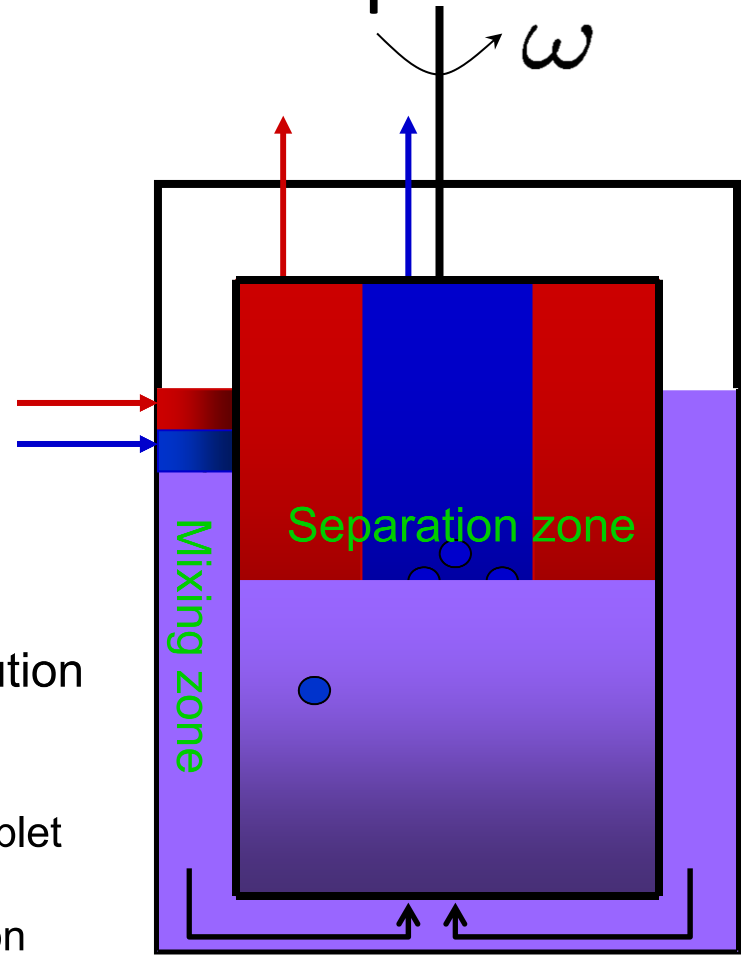
- Turbulent shear
- Breakup, mass transport
- Population balance model developed

$$\frac{\partial n(v)}{\partial t} = v^{-1}\int_0^1 g(s)\,R'(v/s)\,M_1(v/s,t)\,ds - n(v,t)R(v)$$

$$M_1(v,t) = \int_v^\infty v_1\,n(v_1)\,dv_1$$

breakup rate $R(v)$

daughter drop distribution $G(v, v_1)$

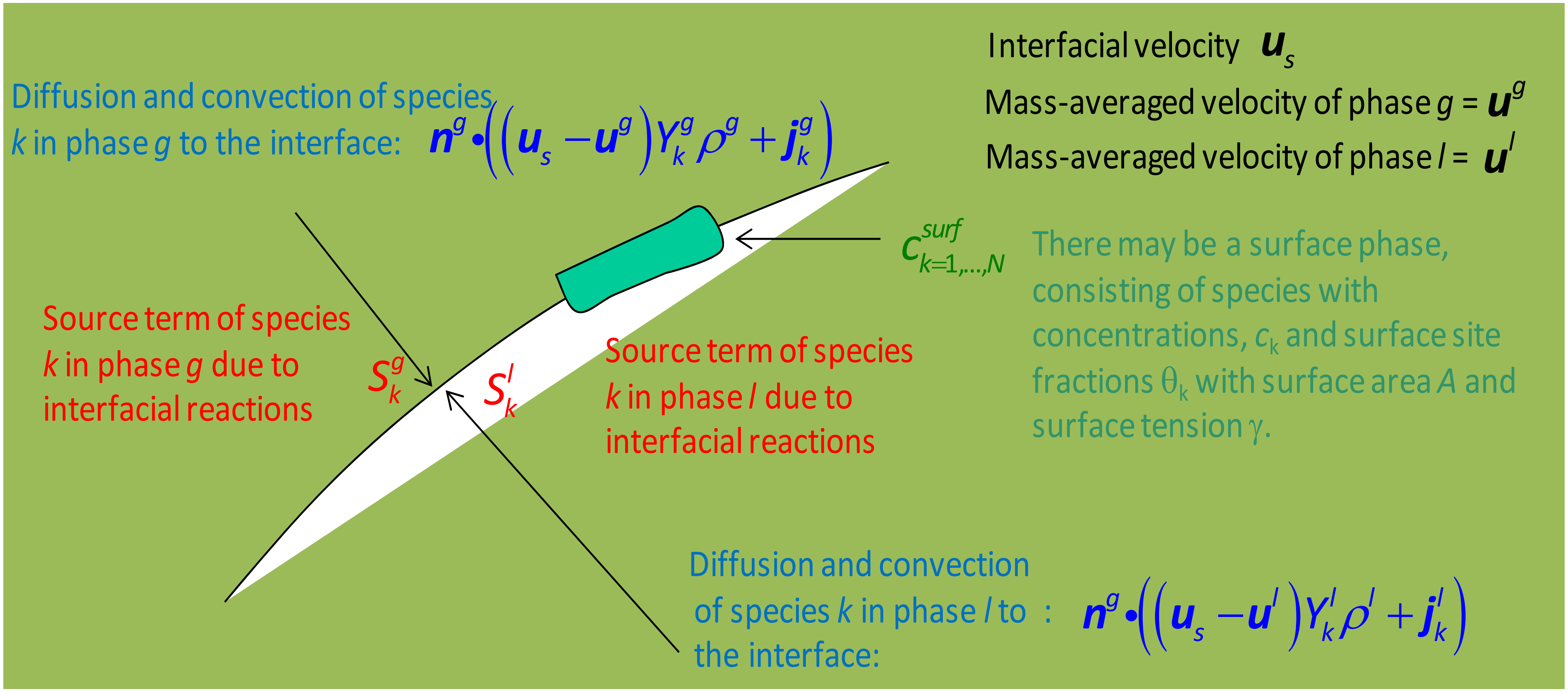


- Proceeding paper completed summarizing the droplet size distribution
- Chemical Engineering Science article in preparation
- Extension to mass transport is next step

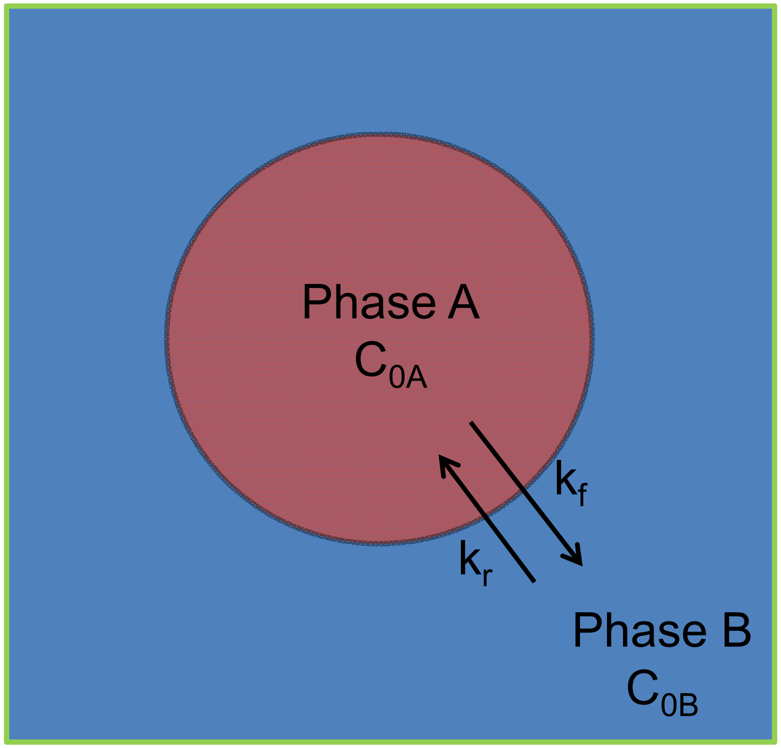
continuous phase: dense fluid

dispersed phase: less dense fluid

A Formalism Developed for Interfacial Mass Transport



Mass Flux Across the Interface



$$Flux = k_f C_{0A} - k_r C_{0B}$$

$$k_f, k_r = \text{Constants}$$

$$C_{0A} = \text{Concentration of species 0 in phase A at the interface}$$

$$C_{0B} = \text{Concentration of species 0 in phase B at the interface}$$

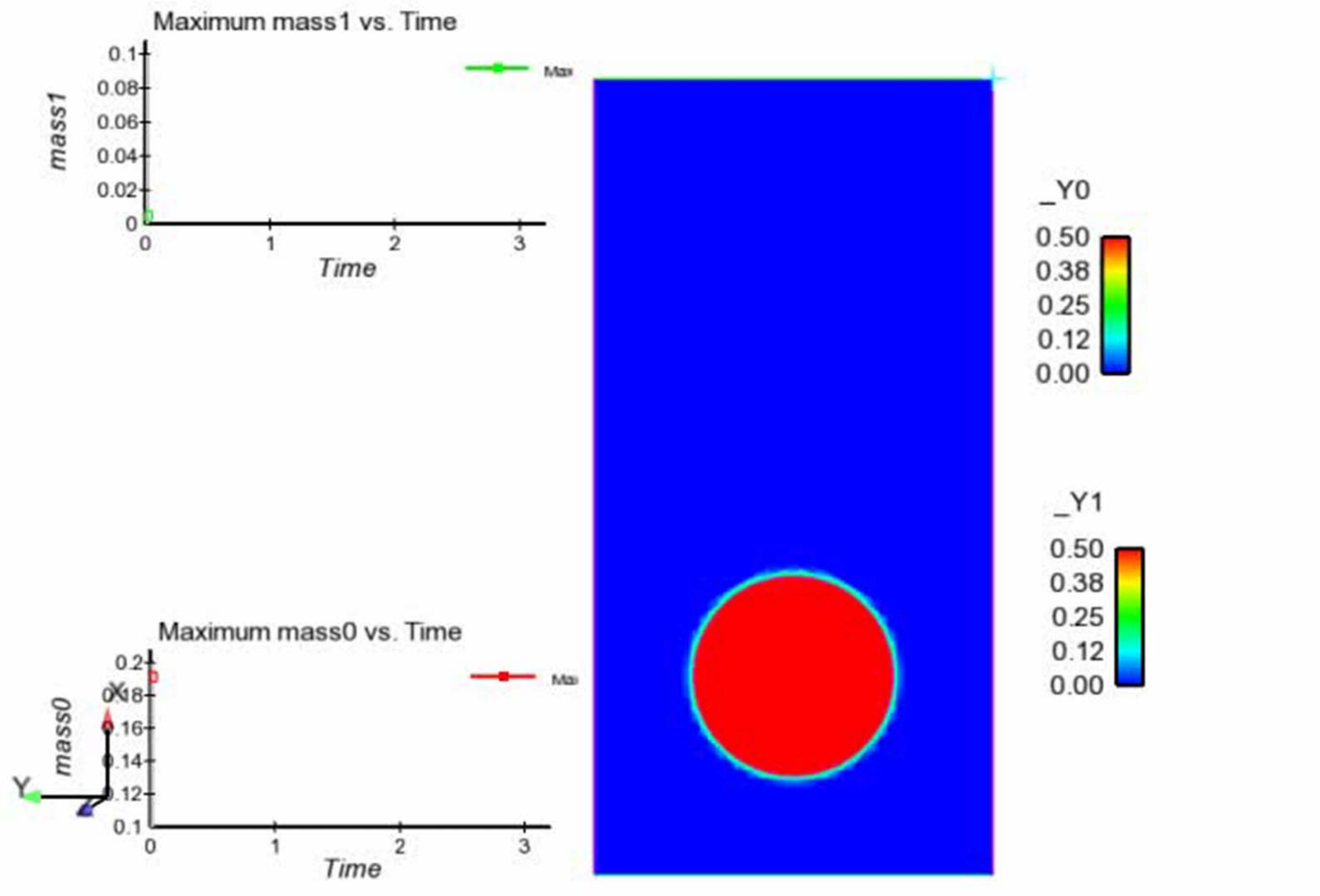
- Species diffuse and advect on either side of the interface and experience a jump in concentration at the interface
- This is natural to implement with CDFEM

Example Problem: Interfacial Mass Transfer with Moving Interface

Interfacial, initial conditions, and properties

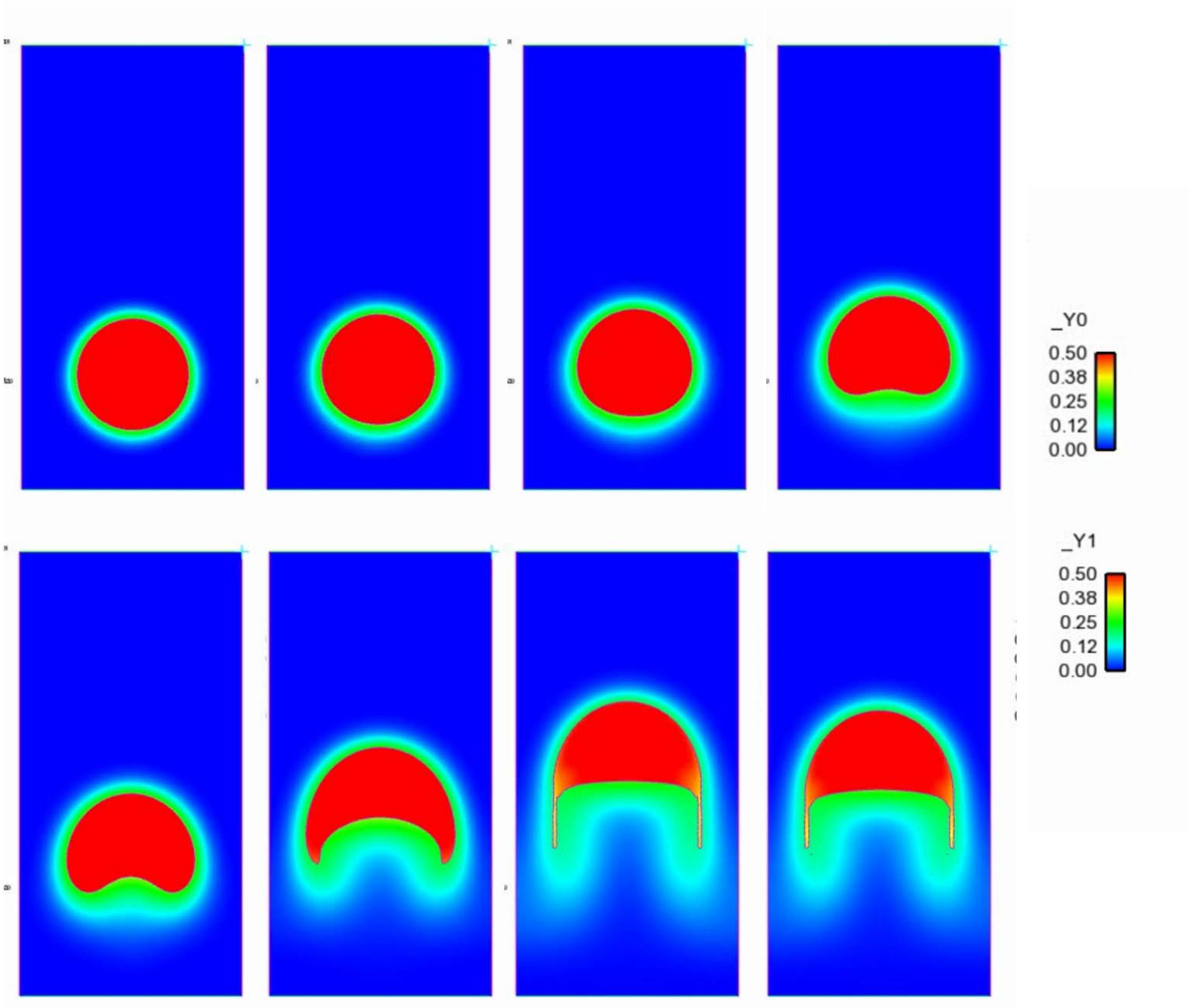
$$D_{0A}\nabla C_0 = k_f C_0 - k_r C_1$$
$$D_{1B}\nabla C_1 = -(k_f C_0 - k_r C_1)$$
$$k_f = 1,\ k_r = 2$$
$$D_{0A} = D_{1B} = 0.05$$
$$C_0^{init} = 1,\ C_1^{init} = 0$$

$$\text{mass0} = \int_{phaseA} C_0\,dxdy$$
$$\text{mass1} = \int_{phaseB} C_1\,dxdy$$



CDFEM implementation allows easy application of concentration jumps

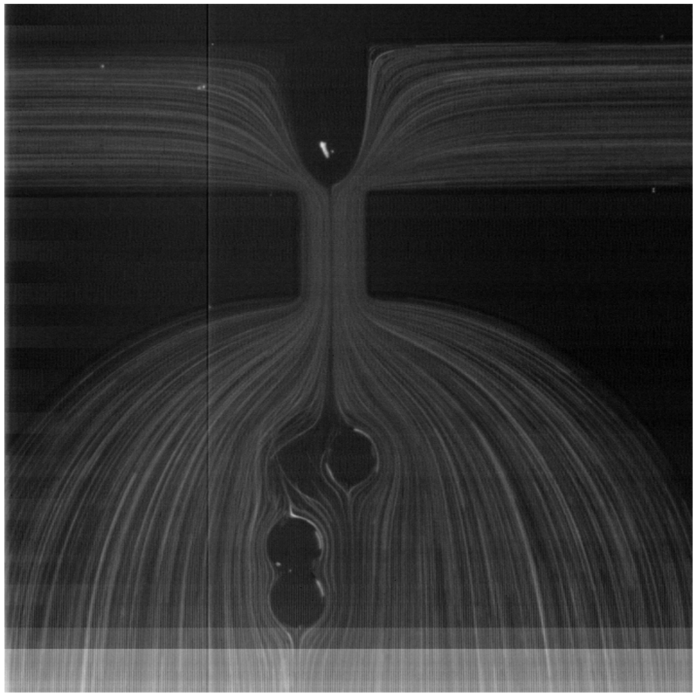
Mass transport with advection

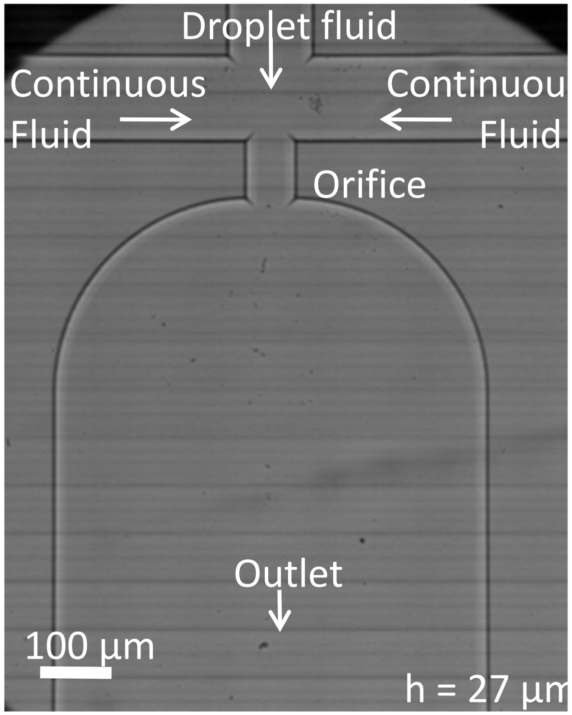


Droplet-scale Experiment in Microfluidic Device

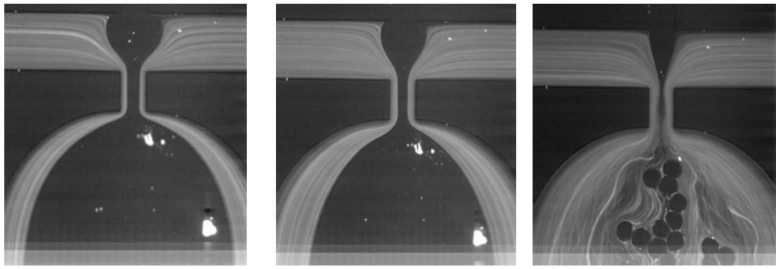
Goals:

- Create uniformly sized droplets
  - ➢ *Flow Focusing Microchannel*
- Understand flow field inside/around droplets
  - ➢ *Phantom high speed camera*
- Understand liquid-liquid mass transfer
  - ➢ *Ocean Optics spectrophotometer*



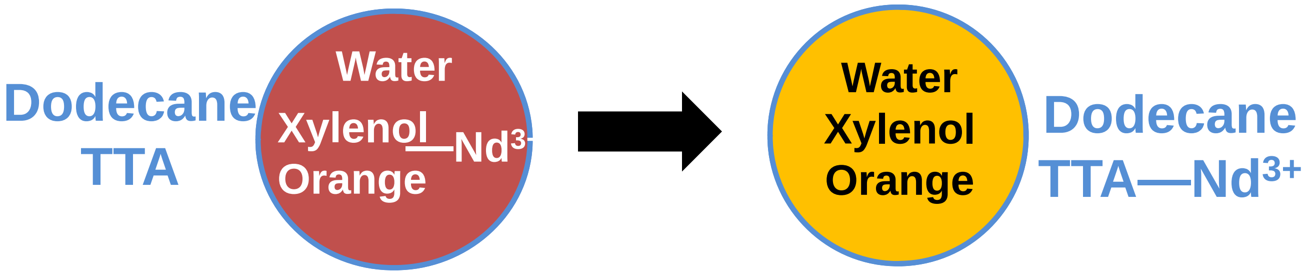


Decreasing inner flow rate

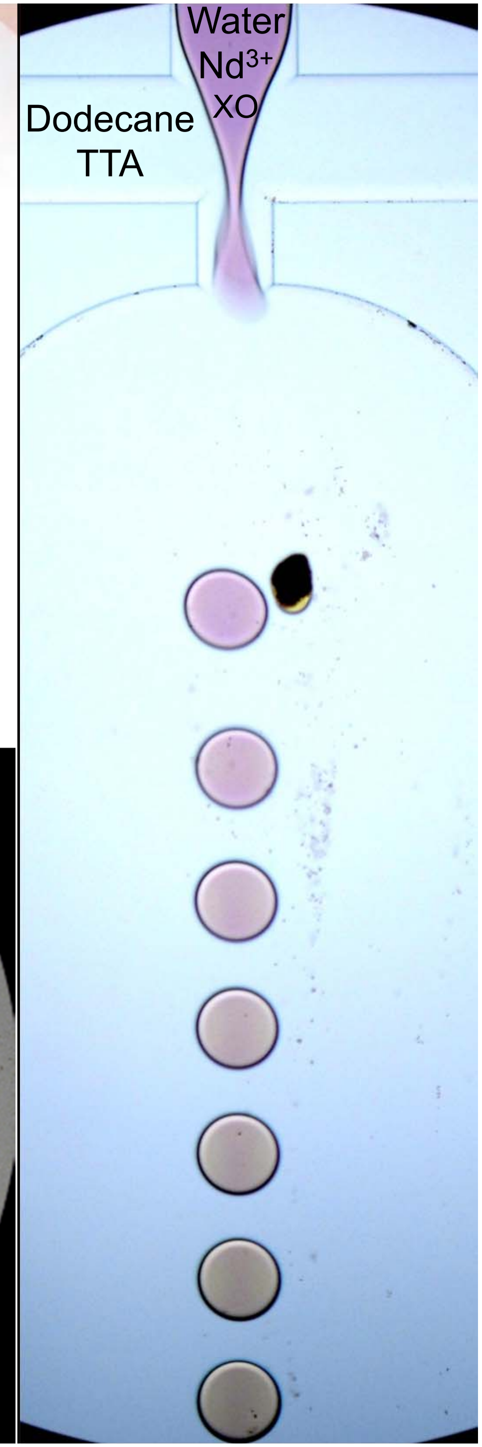


Model System Developed for Mass Transfer Validation

- A nonradioactive model system was chosen based on Nd, which has behavior similar to Pu/U



- A spectrophotometer is used to watch Nd^{3+} transfer from the water to the dodecane

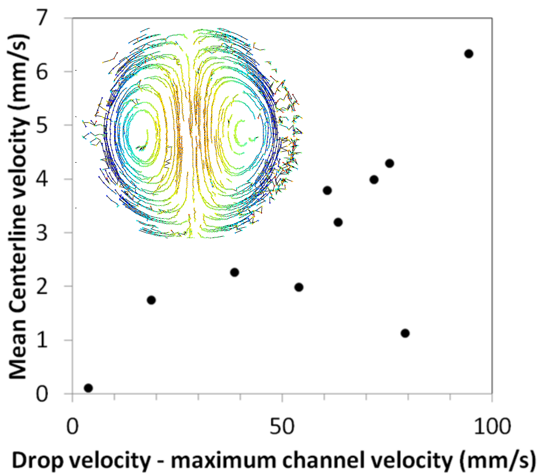


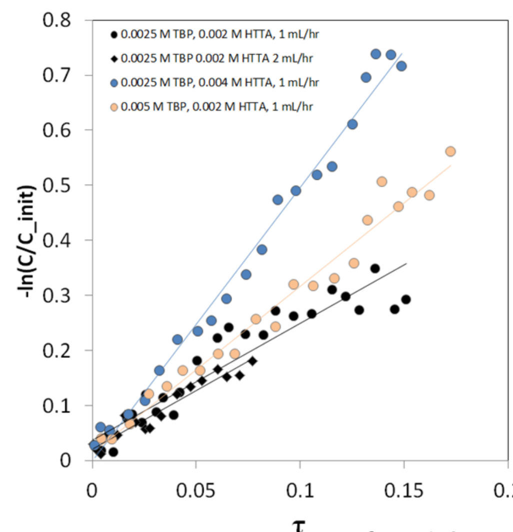
Droplet Scale Experiments

Monodisperse drop generation in a flow-focusing microfluidic chip studied: Droplet size correlated with flow, fluid conditions.

C. C. Roberts, R. Rao, A. Grillet, C. Jove-Colon, C. Brooks, M. Nemer, Lab Chip, 2012, 12 (8): 1540

Flow interior to the droplets visualized using particle tracking.





Model system mimics processing: Concentration quantified by color

$Nd(XO)^{(aq)} + 3\ HTTA^{(o)} + 2\ TBP^{(o)} \leftrightarrow TBP(TTA)_3(TBP)_2^{(o)} + 3\ H^{+(aq)} + XO^{(aq)}$

Mass transfer coefficients measured for numerous flow rates, species concentrations to aid understanding contactor experiments.

Presented: AIChE 2011, 2012; APS DFD 2011. Manuscript in preparation.

Advanced Thermodynamics Model Developed For PUREX Extraction

Reactions Considered for the HNO_3-UO_2-H_2O-TBP-AMSCO

- Log K from extraction and solubility data

$$TBP \bullet HNO_{3(org)} \rightleftarrows H^+ + NO_3^- + TBP_{org} \quad \text{Log K= 0.0228}$$

$$(TBP)_2 \bullet HNO_{3(org)} \rightleftarrows H^+ + NO_3^- + 2TBP_{org} \quad \text{Log K= -0.9}$$

$$TBP_{aq} \rightleftarrows TBP_{org} \quad \text{Log K= 2.8097}$$

$$TBP \bullet H_2O_{(org)} \rightleftarrows TBP_{org} + H_2O \quad \text{Log K= -0.5539}$$

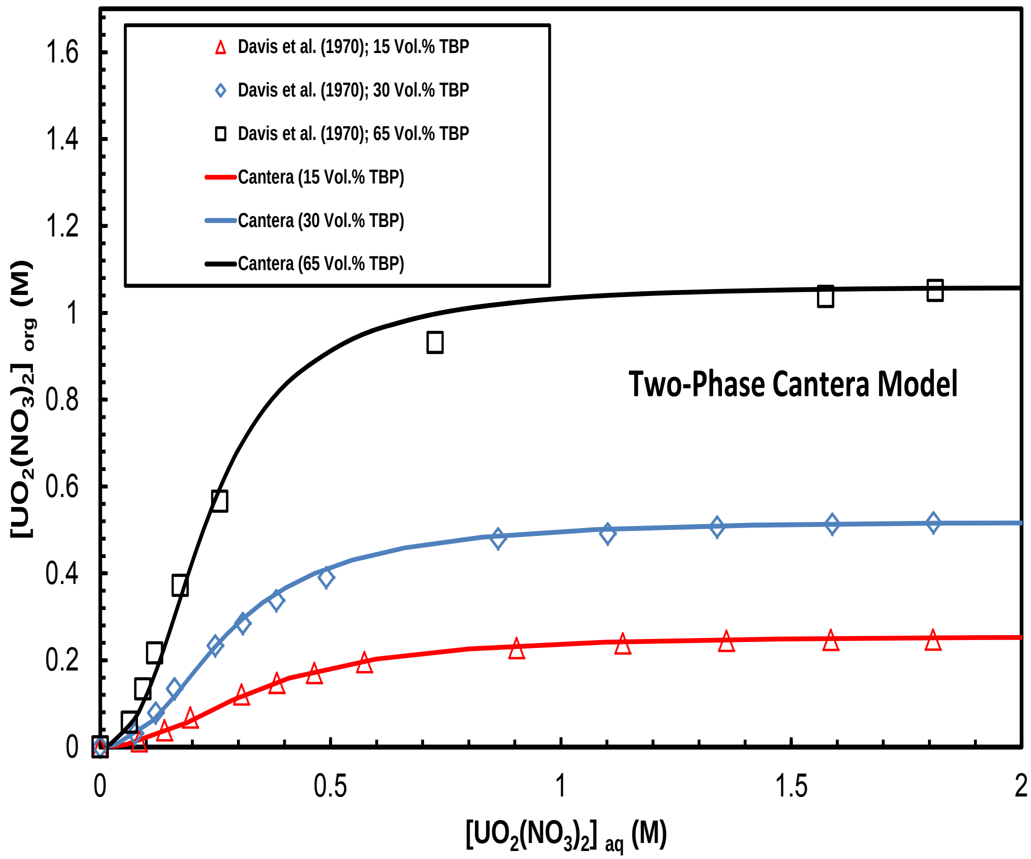
$$(TBP)_{2org} \rightleftarrows 2TBP_{org} \quad \text{Log K= 1.4089}$$

- Reactions for the extraction of U and Pu nitrates by TBP

$$(TBP)_2 \bullet UO_2(NO_3)_{2(org)} \rightleftarrows UO_2^{++} + 2NO_3^- + 2TBP_{org} \quad \text{Log K = -3.4232}$$

$$(TBP)_2 \bullet Pu(NO_3)_{4(org)} \rightleftarrows Pu^{++++} + 4NO_3^- + 2TBP_{org}$$

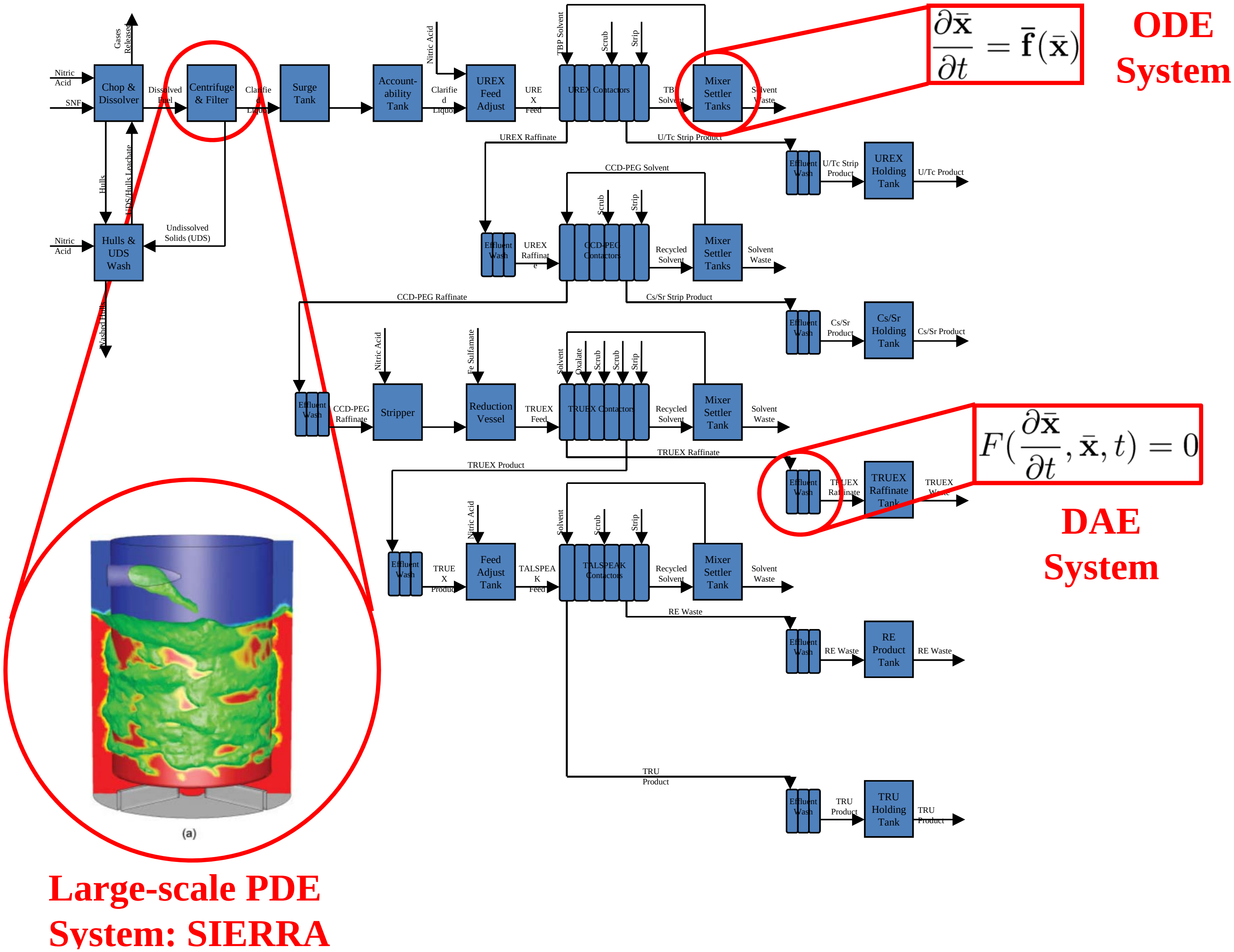
Extraction of Uranyl Nitrate by TBP/AMSCO



- Reaction set built in Cantera based on experimental data
- Cantera coupled to Dakota to determine Gibb's free energies for each species
- Proceedings paper and SAND report completed.
- Journal article submitted to *Separations Science and Technology*
- Cantera included as a library in Sierra Mechanics

Mixed-Fidelity Plant Scale Model

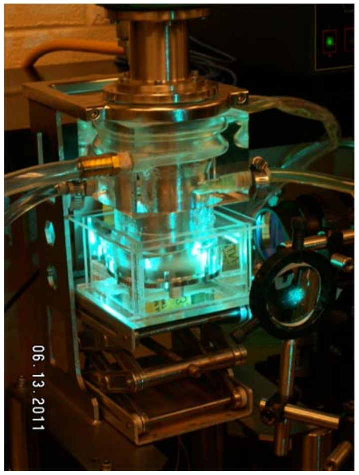
(Embedded technology → UQ, Optimization, Bifurcation Analysis)



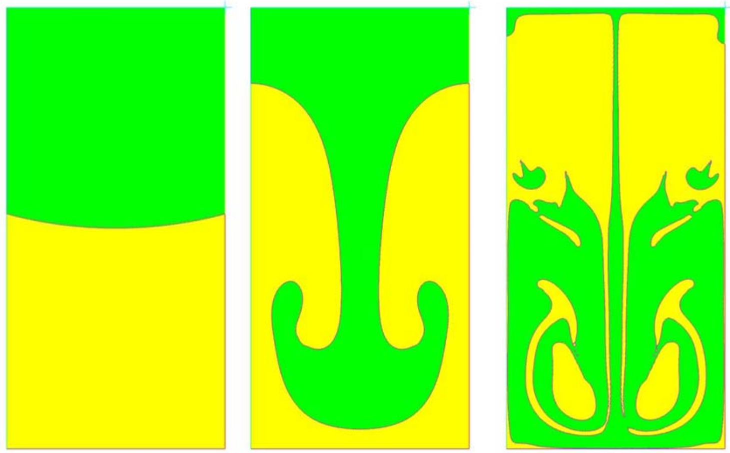
Accomplishments and Future Work

- Droplet-scale model using CDFEM have been developed and verified on a published 2D benchmark problem from Hysing et al, 2009
- Mass transport has been incorporated into the CDFEM model
- A nonradioactive model system was developed using Nd and xylenol orange, with a new spectrophotometer to give quantitative mass transport data for the validation study
- A quantitative droplet-scale mass transport validation experiment is underway using the spectrophotometer
- Advanced thermodynamic models have been developed for the Uranyl Nitrate system and are under development for the Nd system
- Single-phase turbulent contactor simulations have been completed
- Working towards modeling two-phase flow in a centrifugal contactor using first a diffuse level set method and then CDFEM
- Collaboration with Marianne Francois (LANL) for DOE/NEAMS
- Hired post-docs Christine Roberts, Nick Wyatt and staff Martin Nemer
- Network modeling and criticality modeling will be a focus of next FY

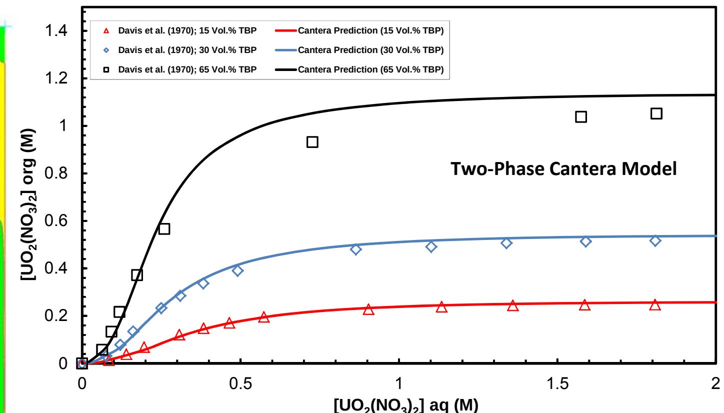
Selected Highlights



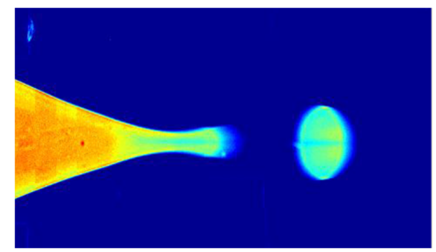
Contactor with laser light sheet to distinguish bubbles and drops

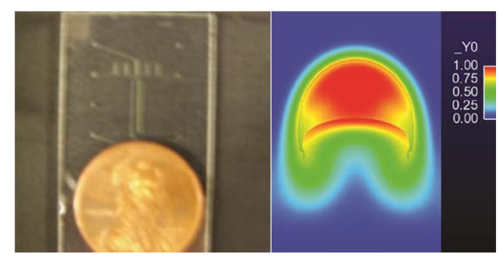


Novel CDFEM algorithm is robust through entire Rayleigh-Taylor instability

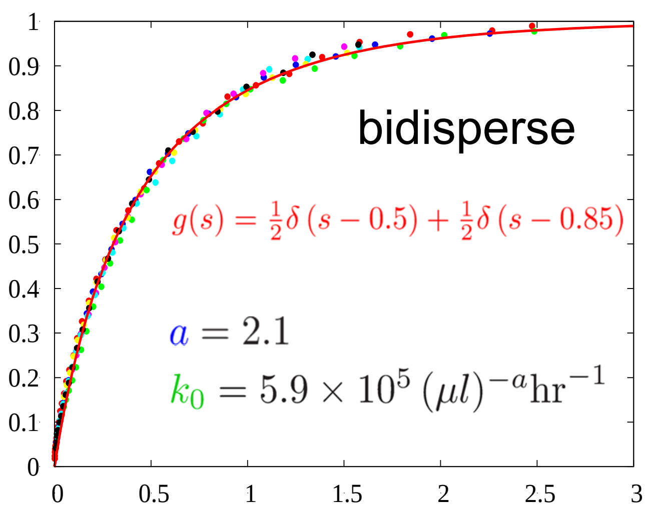


Cantera thermo model developed for U separation in the presence of TBP and H+

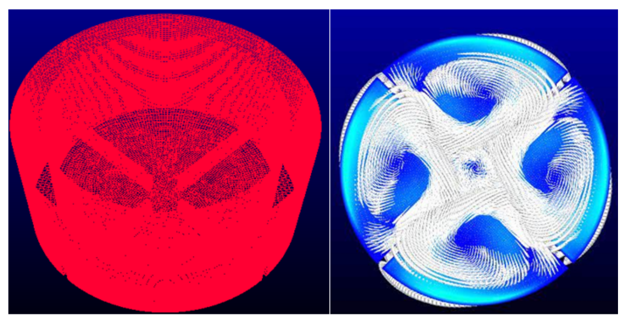




Microfluidic device for quantitative mass transport experiments shown with model



Population balance models predicts break-up data for classic experiment



Sierra/Aria 3D transient turbulent model of contactor