SAND2022-4767C

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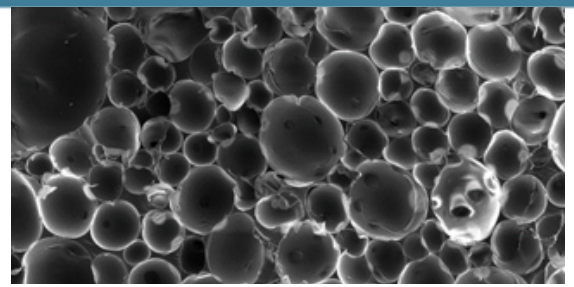
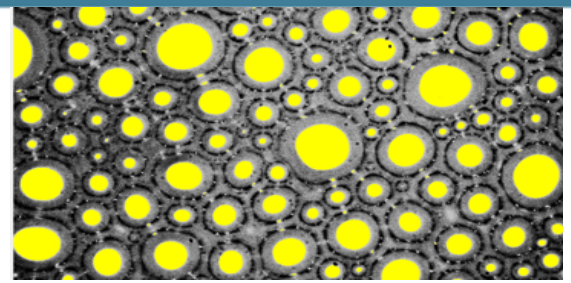
Population Balance Modeling of Foams and Emulsions





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Rising Stars Workshop 2022,

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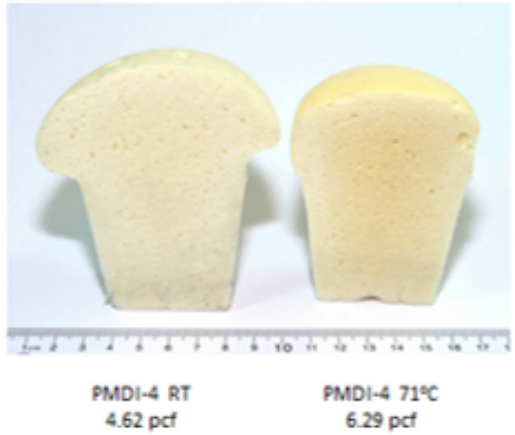
Motivation: Polyurethane Foams

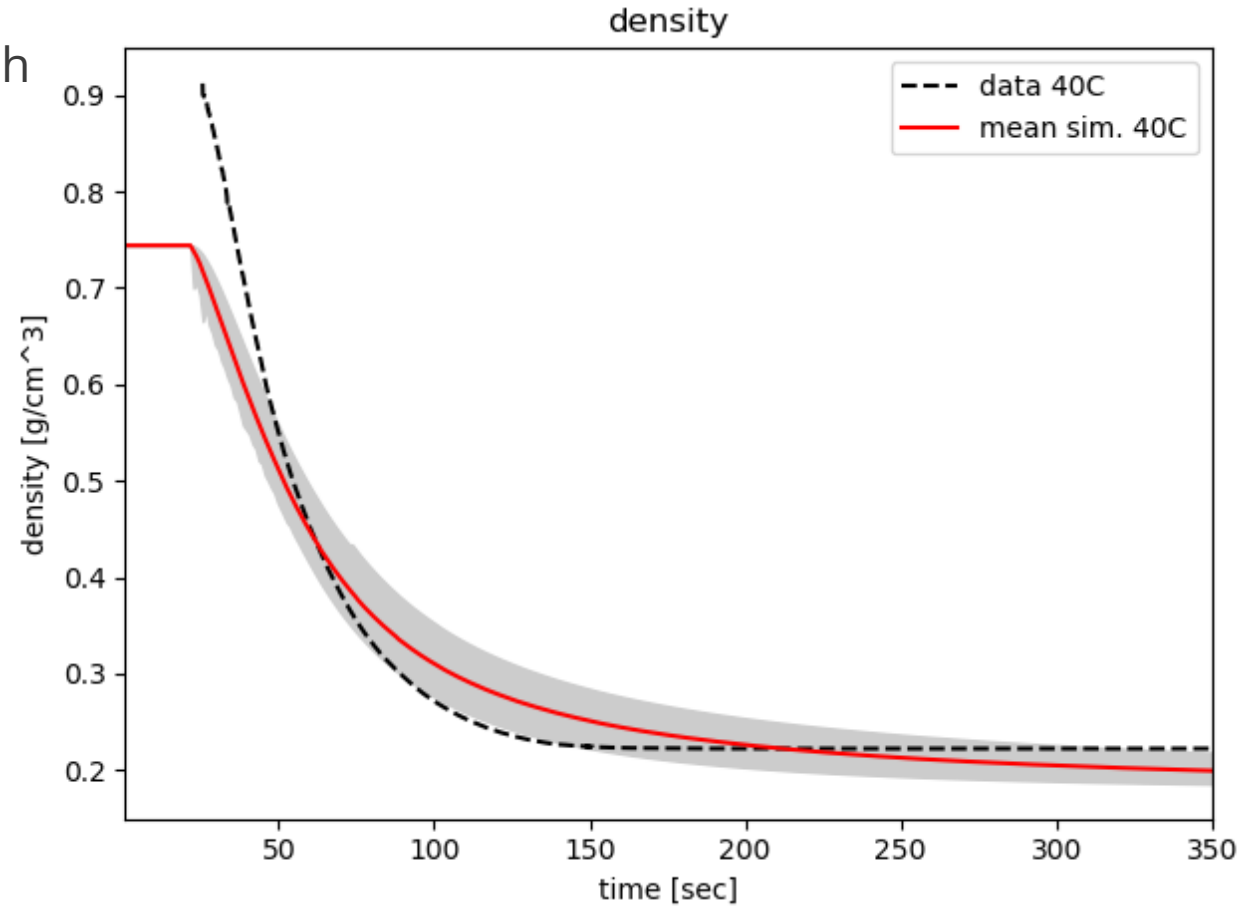
- **Polyurethane foams posses a variety of advantageous qualities including, durability, low thermal conductivity, a high strength-to-weight ratio, and are highly customizable**
- **Can be used to create almost any combination of shape and firmness**
- **Applications include: Insulation (buildings, electronics, appliances, etc.) and cushioning (vehicles, furniture, etc.)**



Goal: a computational model to optimize parts manufacturing and predict material properties

Previous Work Modeling Polyurethane Foam

- Rao et al developed a kinetics based model which tracked the curing reaction through extent of reaction
- Ortiz et al added a population balance equation to Rao et al's model, which included coalescence and growth, but not nucleation



We build on Ortiz et al's and Rao et al's work to include both nucleation and breakage in the population balance equation

[1] Ortiz, Weston, et al. "Population balance modeling of polyurethane foam formation with pressure-dependent growth kernel." *AIChE Journal*. 2022.

[2] Rao, Rekha, et al. "Density predictions using a finite element/level set model of polyurethane foam expansion and polymerization." *Computers & Fluids* 2018.

[3] Rao, Rekha, et al. "The kinetics of polyurethane structural foam formation: Foaming and polymerization." *AIChE Journal*, 2017.

Modeling Polyurethane Foams

System of Equations:

$$\nabla \cdot \boldsymbol{u} = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial t} + \boldsymbol{u} \cdot \rho\right) \quad \text{(conservation of mass)}$$

$$\rho\left(\frac{\partial \boldsymbol{u}}{\partial t} + \boldsymbol{u} \cdot \nabla \boldsymbol{u}\right) = \nabla \cdot T_f + \rho \boldsymbol{g} + f_\Gamma \quad \text{(conservation of momentum)}$$

$$\frac{\partial \xi}{\partial t} + \boldsymbol{u}\nabla\xi - D_\xi \nabla^2 \xi = k(b + \xi^m)(1 - \xi)^n \quad \text{(extent of reaction)}$$

$$\rho C_p\left(\frac{\partial T}{\partial t} + \boldsymbol{u} \cdot \nabla T\right) - \nabla \cdot \lambda \nabla T = \Delta H_{rxn} Y \rho \frac{\partial \xi}{\partial t} \quad \text{(conservation of energy)}$$

$$\frac{\partial C_{H_2O}}{\partial t} + \boldsymbol{u} \cdot \nabla C_{H_2O} - D_{H_2O}\nabla^2 C_{H_2O} = -\, k_{H_2O} C^p_{H_2O}$$

$$\frac{\partial C^{liq}_{CO_2}}{\partial t} + \boldsymbol{u} \cdot \nabla C^{liq}_{CO_2} - D^{liq}_{CO_2}\nabla^2 C^{liq}_{CO_2} = k_{H_2O} C^p_{H_2O} - \overline{G_1}\frac{P}{RT}$$

$$\frac{\partial C^{gas}_{CO_2}}{\partial t} + \boldsymbol{u} \cdot \nabla C^{gas}_{CO_2} - D^{gas}_{CO_2}\nabla^2 C^{gas}_{CO_2} = \overline{G_1}\frac{P}{RT} \quad \text{(conservation chemical species)}$$

symbol	meaning
ρ	*density*
$\boldsymbol{u}$	*mass-average fluid velocity*
T_f	*stress tensor*
f_Γ	*surface tension*
ξ	*extent of reaction*
k	*rate constant*
D_i	*diffusion coefficient for variable i*
b, m, n, p	*fitting parameters*
λ	*thermal conductivity*
T	*temperature*
Y	*liquid mass fraction*
H_{rxn}	*heat of reaction*
C_i	*concentration of variable i*
P	*pressure*
R	*universal gas constant*
$\overline{G_1}$	*growth of moment 1*

Population Balance Equation (PBE)

A continuity statement written in terms of a number density function, $n(t, \boldsymbol{x}, \xi)$ [5, 6]

$$\frac{\partial n}{\partial t} + \nabla_{\boldsymbol{x}} \cdot (n(\xi)\boldsymbol{u}_x) + \nabla_{\xi} \cdot (n(\xi)\boldsymbol{u}_{\xi}) = h(t, \boldsymbol{x}, \xi)$$

- Considered as a function of time t, physical space **x**, and **phase space ξ**
- **Phase space** — a vector of intrinsic properties (e.g. mass, volume, velocity, etc.)
- Processes that impact *n(t, x, ξ)*: growth, shrinkage, coalescence (aggregation), breakage, nucleation, evaporation

[5] Marchisio, Daniele L., and Rodney O. Fox. *Computational models for polydisperse particulate and multiphase systems*. Cambridge University Press, 2013.
[6] Ramkrishna, Doraiswami. *Population balances: Theory and applications to particulate systems in engineering*. Elsevier, 2000.

PMDI-10 included phenomena

— Model a continuous liquid phase with a gaseous disperse phase (bubbles) which cures over time

— Model PMDI-10 filling a 3D cylindrical mold

— Phase space property: bubble volume, $\xi=\nu$

Consider the following PBE: $$\frac{\partial n(\nu)}{\partial t} + \nabla \cdot (n(\nu)\boldsymbol{u}) + \frac{\partial}{\partial \nu}\left(n(\nu)G(\nu)\right) = S(\nu,\nu') + \boldsymbol{B}(\boldsymbol{\nu}) + \boldsymbol{J}(\boldsymbol{t})$$

- Bubble size distribution n(ν) — distribution on bubble volume ν
- Growth term G(ν) — how bubbles of volume ν grow
- Coalescence term S(ν, ν') — how bubbles of volume ν and ν' form a bubble of volume $\nu + \nu'$
- **Breakage B(ν) term** — how bubbles of volume ν break
- **Nucleation term J(t)** — how new bubbles appear, separate from previous processes
- Bubble velocity **u** — assumed to be the same as the fluid velocity

PMDI-10 continued

Population Balance Equation:

$$\frac{\partial n(v)}{\partial t} + \nabla \cdot (n(v)\boldsymbol{u}) + \frac{\partial}{\partial v}\left(n(v)G(v)\right) = S(v,v') + B(v) + J(t)$$

Source terms:

- **Coalescence term:** $S(v,v') = \frac{1}{2}\int_0^v \beta(v, v-v')n(v)n(v-v')dv' - \int_0^\infty \beta_p(v,v')n(v)n(v')dv'$
- **Breakage term:** $B(v) = \int_v^\infty a(v')b(v|v')n(v')dv' - a(v)n(v)$

Kernels for PBE terms

Growth kernel:[1]

$$G_p(v) = C_0 \left(\frac{P_{atm}^2}{(P - P_{ref})^2} \right) \frac{\eta_{ref}}{\eta}$$

Coalescence kernel:[4]

$$\beta_p(v, v') = \beta_0(v + v')$$

Breakage kernel:[7]

$$a(v) = a_0 v^{\alpha}$$

Fragment distribution :[7]

$$b(v|v') = \begin{cases} 2 & if \quad v = \frac{v'}{2} \\ 0 & else \end{cases}$$

Nucleation term:

$$J = J_0 \max\left(0, \frac{w_c - w_{max}}{w_{max}}\right)$$

symbol	meaning
C_0	*growth rate constant*
P	*pressure*
P_{atm}	*atmospheric pressure*
P_{ref}	*reference pressure*
η	*viscosity*
η_{ref}	*reference viscosity*
β_0	*coalescence rate constant*
a_0	*breakage rate constant*
α	*breakage exponent*
J_0	*nucleation rate constant*
w_c	*current weight fraction of* CO_2
w_{max}	maximum weight fraction CO_2

[1] Ortiz, Weston, et al. "Population balance modeling of polyurethane foam formation with pressure-dependent growth kernel." *AIChE Journal*. 2022.
[4] Karimi, Mohsen, and Daniele L. Marchisio. "A baseline model for the simulation of polyurethane foams via the population balance equation." *Macromolecular Theory and Simulations*. 2015.
[7] Marchisio, Daniele L., R. Dennis Vigil, and Rodney O. Fox. "Quadrature method of moments for aggregation–breakage processes." *Journal of colloid and interface science*. 2003.

Quadrature Method of Moments (QMOM)

Idea: *transform PBE to a discrete set of moment equations, and reconstruct the BSD from the moments*

Moment transformation: [8] $m_k = \int_0^\infty n(v) v^k dv, \quad k = 0, 1, 2, \ldots$

Apply moment transform to PBE: $\frac{\partial m_k}{\partial t} + \boldsymbol{u} \cdot m_k = k G_k + S_k + B_k + J_k \qquad k = 0, 1, 2, 3$

Physical meaning of key moments: $m_0 — \frac{\#\ bubbles}{liquid\ volume}$ $m_1 — \frac{total\ bubble\ volume}{liquid\ volume}$

Estimate integrals with quadrature (ν_i, ω_i)

$$\bar{G}_k = \sum_{i=1}^{N} \omega_i G_p(\nu_i) \nu_i^{k-1}$$

$$\bar{S}_k = \sum_{i=1}^{N} \sum_{j=1}^{N} \omega_i \omega_j \left[(\nu_i + \nu_j)^k - \nu_i^k - \nu_j^k \right] \beta_p(\nu_i, \nu_j)$$

$$\bar{B}_k = \sum_{i}^{N} \omega_i a(\nu_i) 2^{1-k} \nu_i^k - \sum_{i}^{N} \omega_i \nu_i^k a(\nu_i)$$

$$\bar{J}_k = 0^k J_0$$

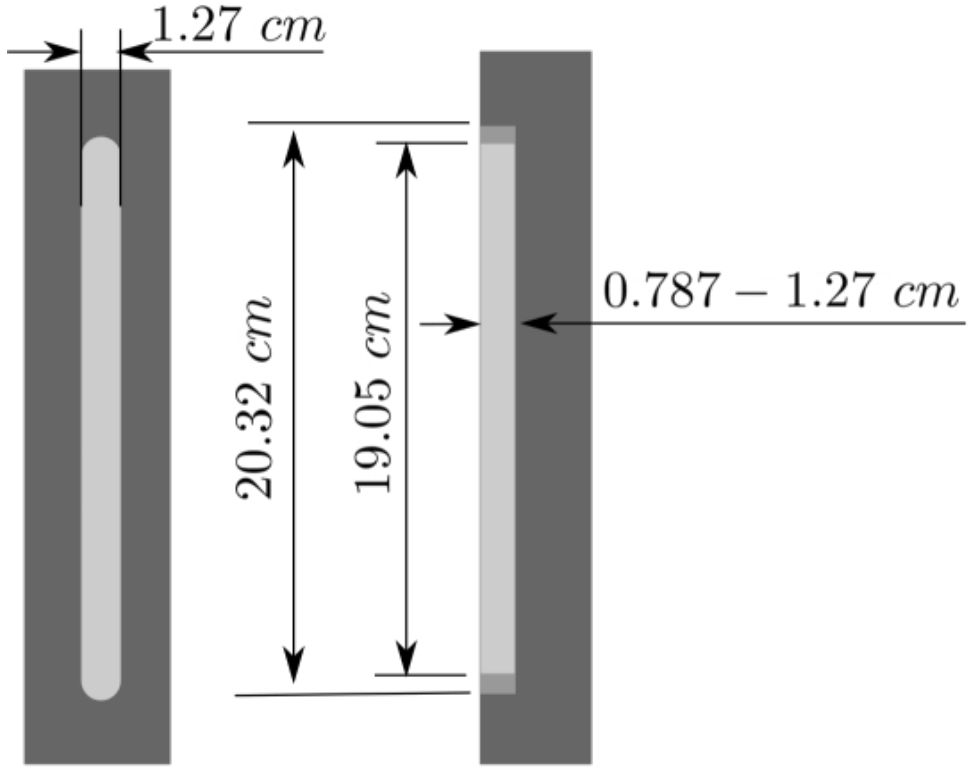
[8] McGraw, Robert. "Description of aerosol dynamics by the quadrature method of moments." *Aerosol Science and Technology*. 1997

[9] Yuan, Cansheng, and Rodney O. Fox. "Conditional quadrature method of moments for kinetic equations." *Journal of Computational Physics*. 2011.

[10] John V, Angelov I, Öncül A, Thévenin D. Techniques for the reconstruction of a distribution from a finite number of its moments. Chem Eng Sci. 2007.

Summary of Numerical Methods

- Arbitrary Lagrangian-Eulerian
- Implicit Euler time integration (except moment source)
- Implemented in the open-source software Goma
- PBE solved via quadrature method of moments (QMOM)
- Nodes and weights found using the Adaptive Wheeler Algorithm[9]
- For *N*-node quadrature we only need 2*N* moment
- Initialize moments assuming log-normal BSD



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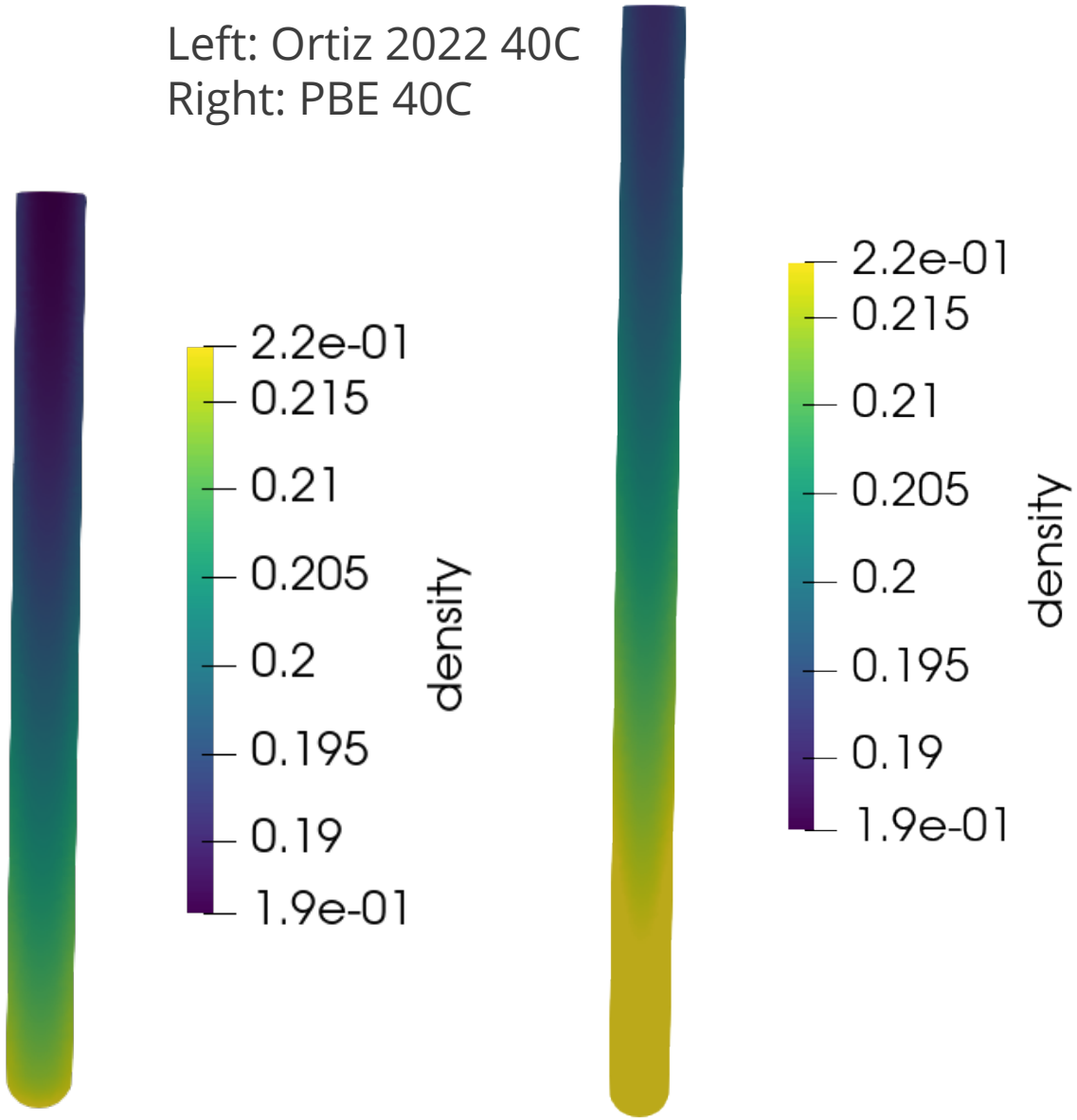
[9]Yuan, Cansheng, and Rodney O. Fox. "Conditional quadrature method of moments for kinetic equations." Journal of Computational Physics. 2011.

Results

Left: Ortiz 2022 40C
Right: PBE 40C



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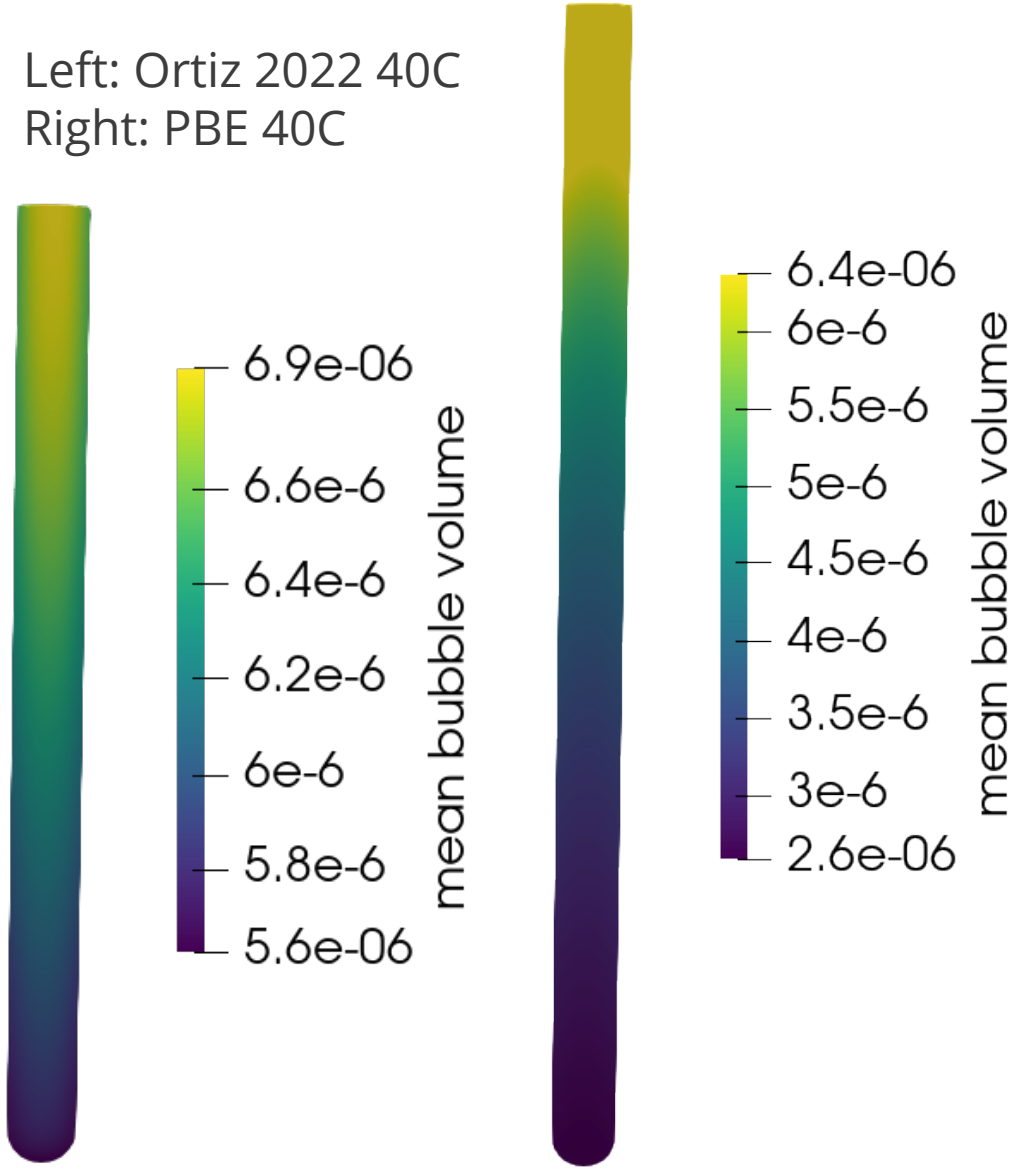
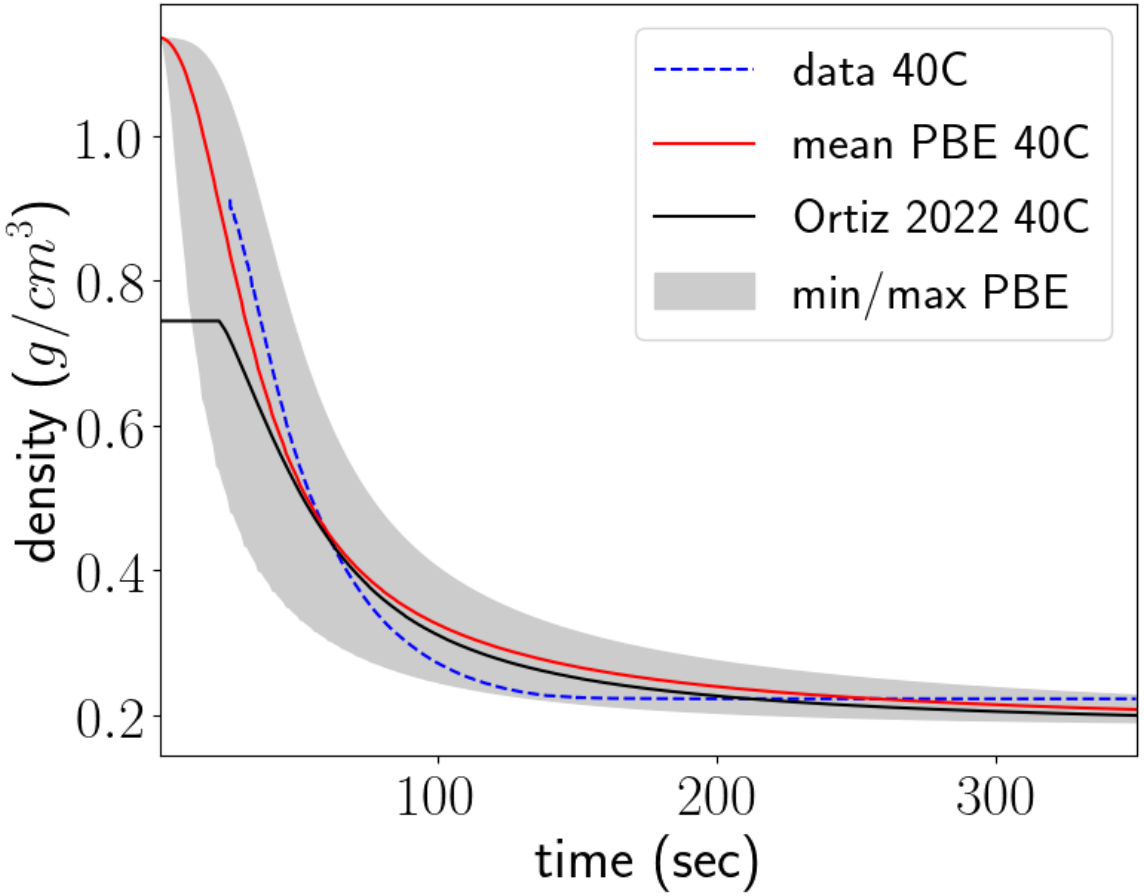
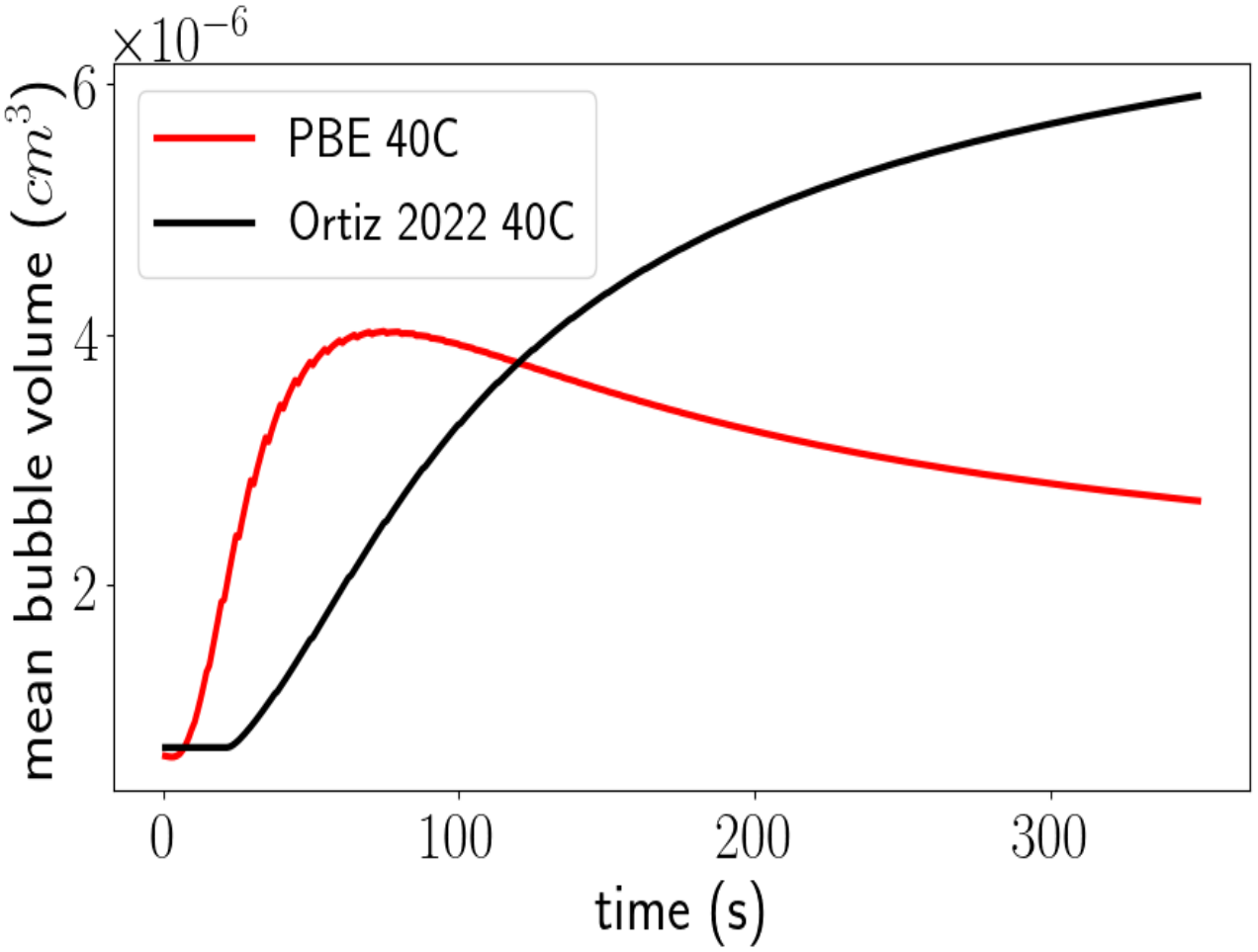


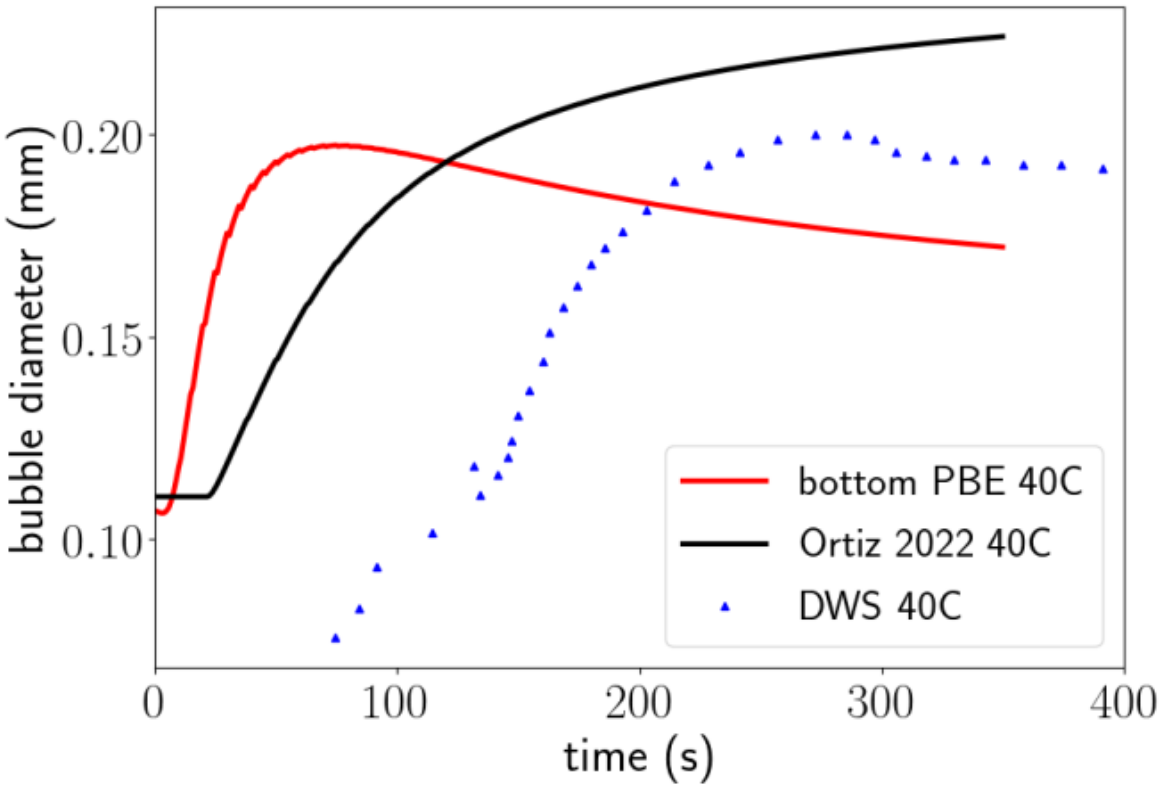
Results Continued

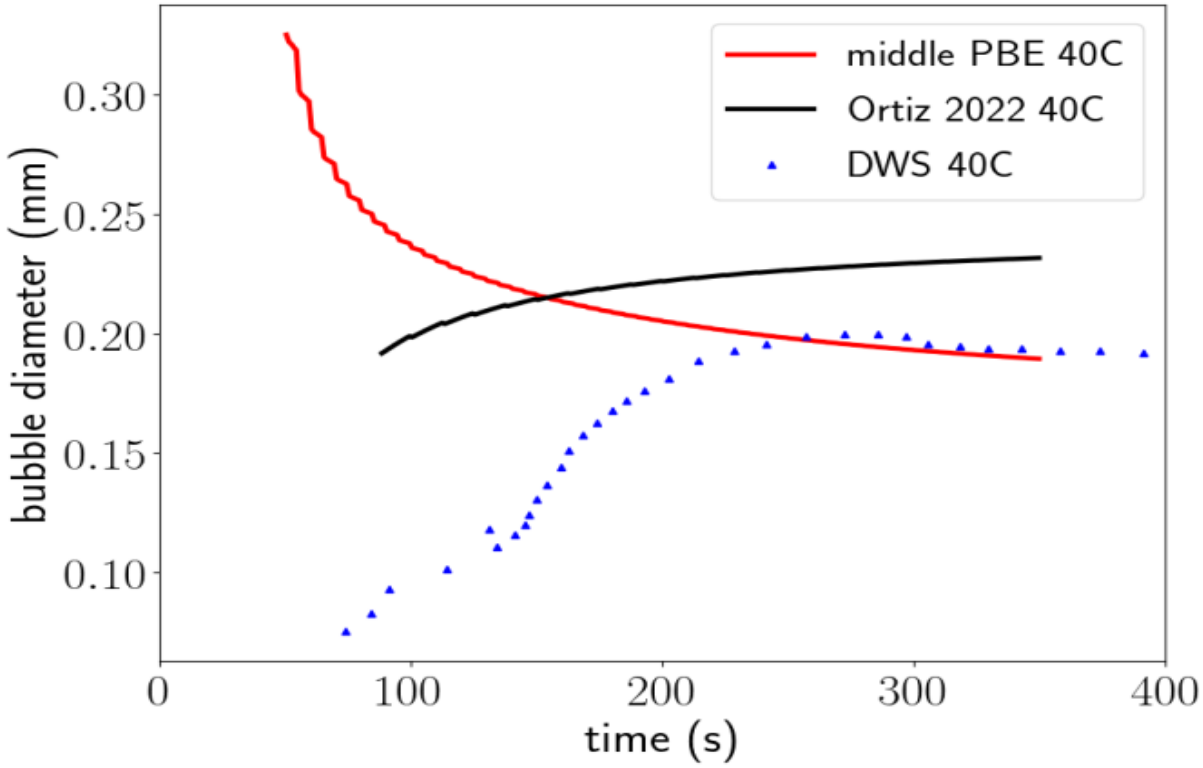




- Capturing early density well and producing similar shape to Ortiz 2022
- Different shape for mean bubble volume over time

Results Continued





Bottom: 2.5cm from base of mold
Middle: 10cm from base of mold
DWS: Diffusion Wave Spectroscopy

PBE bottom closer to shape of DWS data

Summary and Future Work

Summary:

- Added nucleation and breakage kernels to kinetics model with population balance modeling
- Obtaining a better picture of the underlying microstructure

Future work:

- Continue to modify and improve kernels
- Apply population balance model to coarsening data
- Working to implement this framework for polymer upcycling

Works Cited

Texts:

[1]Ortiz, Weston, et al. "Population balance modeling of polyurethane foam formation with pressure-dependent growth kernel." *AIChE Journal*. 2022.

[2]Rao, Rekha, et al. "Density predictions using a finite element/level set model of polyurethane foam expansion and polymerization." *Computers & Fluids* 2018.

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[10]John V, Angelov I, Öncül A, Thévenin D. Techniques for the reconstruction of a distribution from a finite number of its moments. Chem Eng Sci. 2007.

Images/photos:

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https://www.buildinggreen.com/blog/epa-raises-health-concerns-spray-foam-insulation

PU Vacuum Foaming Molds | Refrigerator Door, Cabinet

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Karimi, Mohsen, H. Droghetti, and Daniele L. Marchisio. "PUFoam: A novel open-source CFD solver for the simulation of polyurethane foams." Computer Physics Communications 217 (2017): 138-148.