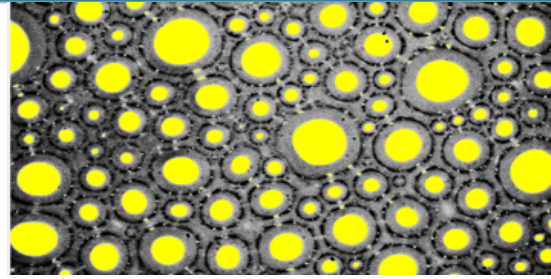
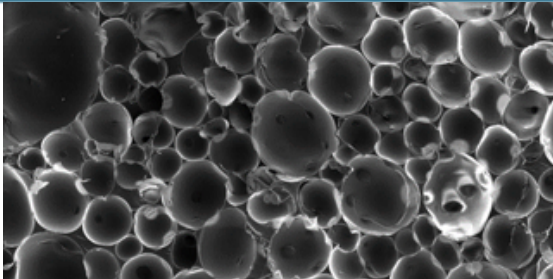




A Coupled Computational Fluid Dynamics/Population Balance Method to Understand Microstructure in Foams and Emulsions



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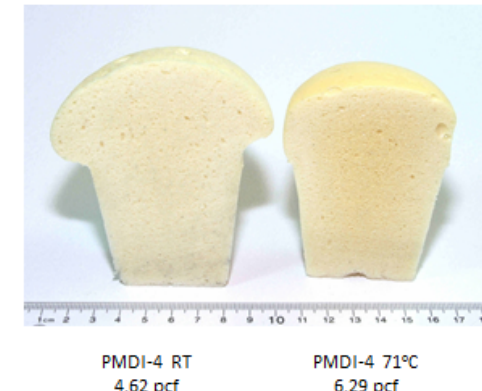
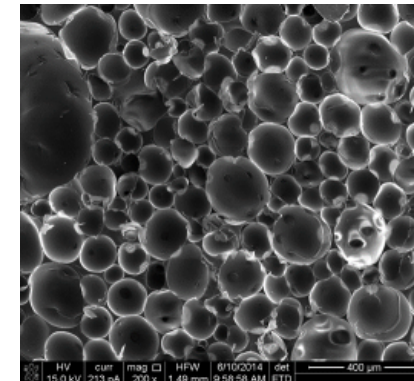
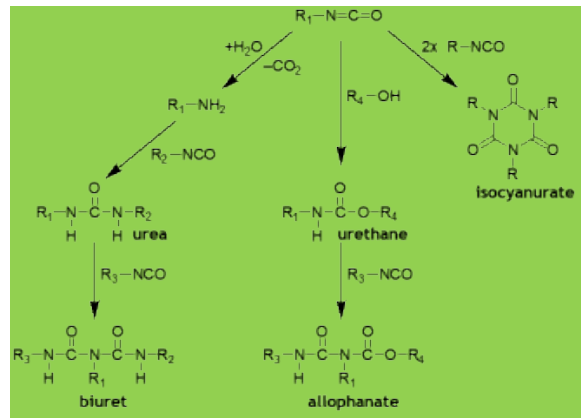
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

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Motivation



- Polyurethane foams are widely used as insulators
- Insulation efficiency is a complex function of gas fraction, solid/gas thermal conductivity, and foam cell size distribution
- A HPC-based polyurethane (PU) foaming model to predict the impact of formulation changes on bubble-scale thermal properties is needed
- A PU model would expedite the timeline for more energy efficient foams and appliances



► Computational models can help produce more insulating foam with less waste

Cradle-to-Grave Model of PMDI Foam



Overarching Goal: A computational model for foaming, vitrification, curing, aging to help us design molds and determine how inhomogeneities effect the structural response of the final part, including long term shape stability

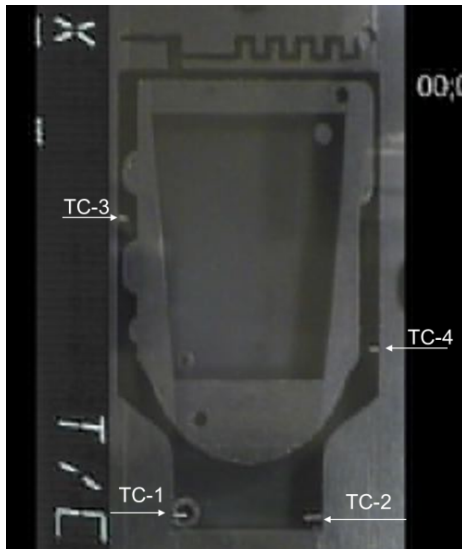


Injection,
foaming and
initial curing
at lower T



Run 030110-PMDI-4 60°C
Free Rise
Sandia National Labs

Oven time
at higher T
to make
sure it is
fully cured



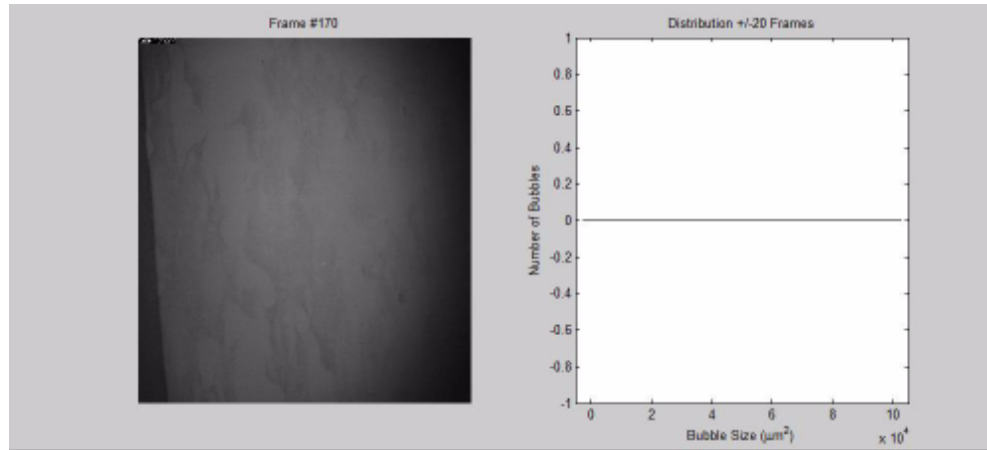
Remove from
mold – predict
cure and
thermal
stresses



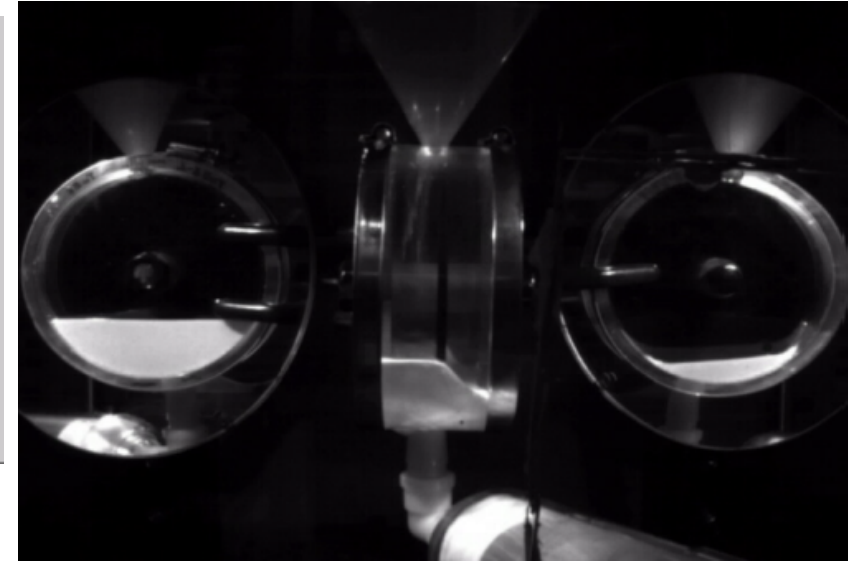
Predict
shape and
size over
years



Foam Filling is Complex



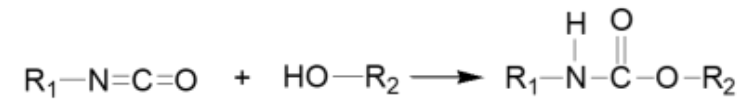
Foam front moving past camera, with bubble sizes at transparent wall determined with image processing.



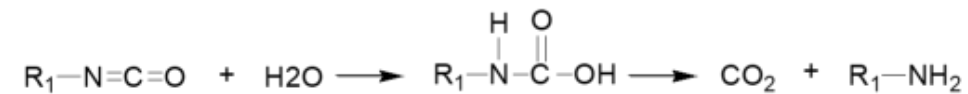
3 views of foam filling with several plates spaced unevenly. Vent location is critical to keep from trapping air.

- Gas generation drives the foam expansion, changing the material from a viscous liquid to a multiphase material.
- Continuous phase is time- and temperature-dependent and eventually vitrifies to a solid.

Two key reactions: Isocyanate reaction with polyols and water



Urethane formation,
crosslinking



Foaming reaction yields
CO₂ and amine

Equations of Motion Include Evolving Material Models



Momentum equation and continuity have variable density, shear viscosity, and bulk viscosity

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\rho \mathbf{v} \cdot \nabla \mathbf{v} - \nabla p + \nabla \cdot (\mu_f (\nabla \mathbf{v} + \nabla \mathbf{v}^t)) - \nabla \cdot \lambda (\nabla \cdot \mathbf{v}) \mathbf{I} + \rho \mathbf{g}$$

$$\frac{D\rho_f}{Dt} + \rho_f \nabla \cdot \mathbf{v} = 0$$

Energy equation has variable heat capacity and thermal conductivity including a source term for heat of reaction for foaming and curing reactions

$$\rho C_{pf} \frac{\partial T}{\partial t} + \rho C_{pf} \mathbf{v} \cdot \nabla T = \nabla \cdot (k \nabla T) + \rho \phi_e \Delta H_{rxn} \frac{\partial \xi}{\partial t}$$

Extent of reaction equation for polymerization: condensation chemistry

$$\frac{\partial \xi}{\partial t} = \left(\frac{1}{(1 + wa)^\beta} \right) \left(k_0 \exp\left(-\frac{E}{RT}\right) \right) (b + \xi^m)(1 - \xi)^n$$

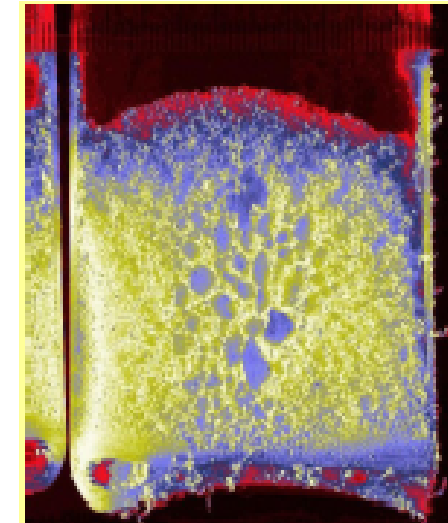
Molar concentration equations for water and carbon dioxide

$$\frac{dC_{H_2O}}{dt} = -k_{H_2O} C_{H_2O}^n$$

$$C_{H_2O} = \frac{\rho_{foam} x_{H_2O}}{M_{H_2O}}$$

$$\frac{dC_{CO_2}}{dt} = +k_{H_2O} C_{H_2O}^n$$

$$C_{CO_2} = \frac{\rho_{foam} x_{CO_2}}{M_{CO_2}}$$



NMR imaging shows coarse microstructure (Altobelli, 2006)

$$k_{H_2O} = A_{H_2O} \exp(-E_{H_2O} / RT)$$

Rao et al., "Polyurethane kinetics for foaming and polymerization", *AIChE Journal*, 2017

Complex Material Models Vary with Cure, Temperature, and Gas Fraction



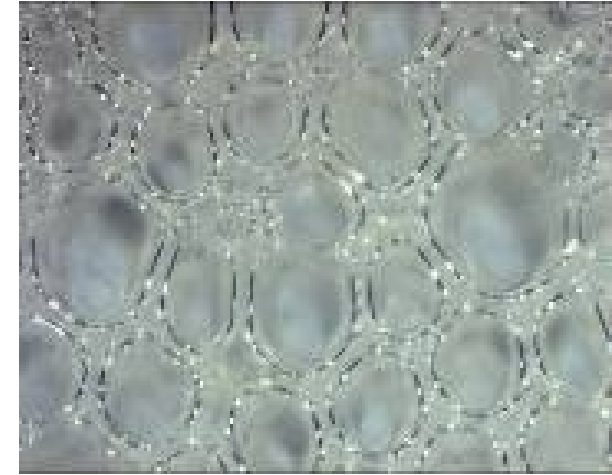
Foaming reaction predicts moles of gas from which we can calculate density

$$\rho_{gas} = \frac{PM_{CO_2}}{RT}$$

$$v = \frac{V_{gas}}{V_{liq}} = \frac{M_{CO_2} C_{CO_2}}{\rho_{gas}} \quad \phi_v = \frac{v}{1+v}$$

$$\rho_{foam} = \rho_{gas} \phi_v + \rho_{liq} (1 - \phi_v)$$

Compressibility built into this model via the ideal gas law for gas density



Foam is a collection of bubbles in curing polymer

Thermal properties depend on gas volume fraction and polymer properties

$$k = \frac{2}{3} \left(\frac{\rho}{\rho_e} \right) k_e + \left(1 - \frac{\rho}{\rho_e} \right) k_v$$

$$C_{pf} = C_{pl} \phi_l + C_{pv} \phi_v + C_{pe} \phi_e$$

Shear and bulk viscosity depends on gas volume fraction, temperature and degree of cure

$$\mu = \mu_0 \exp\left(\frac{\phi_v}{1-\phi_v}\right) \quad \mu_0 = \mu_0^0 \exp\left(\frac{E_\mu}{RT}\right) \left(\frac{\xi_c^p - \xi^p}{\xi_c^p}\right)^{-q}$$

$$\lambda = \frac{4}{3} \mu_0 \frac{(\phi_v - 1)}{\phi_v}$$

M. Mooney, *J. Colloid Sci.*, **6**, 162-170 (1951).

- Experiments to determine foaming and curing kinetics as well as parameters for model

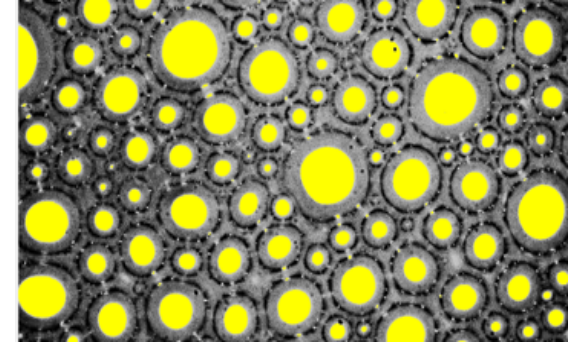
Gibson, L. J.; M. F. Ashby. Cambridge University Press, Cambridge, UK, 1990

Population Balance Equation (PBE)



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

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



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

⁵Marchisio, Daniele L., and Rodney O. Fox. *Computational models for polydisperse particulate and multiphase systems*. Cambridge University Press, 2013

⁶Ramakrishna, Doraiswami. *Population balances: Theory and applications to particulate systems in engineering*. Elsevier, 2000.

Quadrature Method of Moments (QMOM)



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

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

Apply moment transform to PBE:

$$\frac{\partial m_k}{\partial t} + \mathbf{u} \cdot \nabla m_k = k G_k + S_k + B_k + J_k \quad k = 0, 1, 2, 3$$

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

Estimate integrals with quadrature (v_i, ω_i)

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

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

$$\bar{B}_k = \sum_i \omega_i a(v_i) 2^{1-k} v_i^k - \sum_i \omega_i v_i^k a(v_i)$$

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

kernels: rate at which the process takes place

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

⁹John 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.

¹⁰Yuan, Cansheng, and Rodney O. Fox. "Conditional quadrature method of moments for kinetic equations" Journal of Computational Physics. 2011.

Modeling Polyurethane Foams

System of Equations:

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

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

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

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

$$\frac{\partial C_{H_2O}}{\partial t} + \mathbf{u} \cdot \nabla C_{H_2O} - D_{H_2O} \nabla^2 C_{H_2O} = -k_{H_2O} C_{H_2O}^p$$

$$\frac{\partial C_{CO_2}^{liq}}{\partial t} + \mathbf{u} \cdot \nabla C_{CO_2}^{liq} - D_{CO_2}^{liq} \nabla^2 C_{CO_2}^{liq} = k_{H_2O} C_{H_2O}^p - \overline{G_1} \frac{P}{RT}$$

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

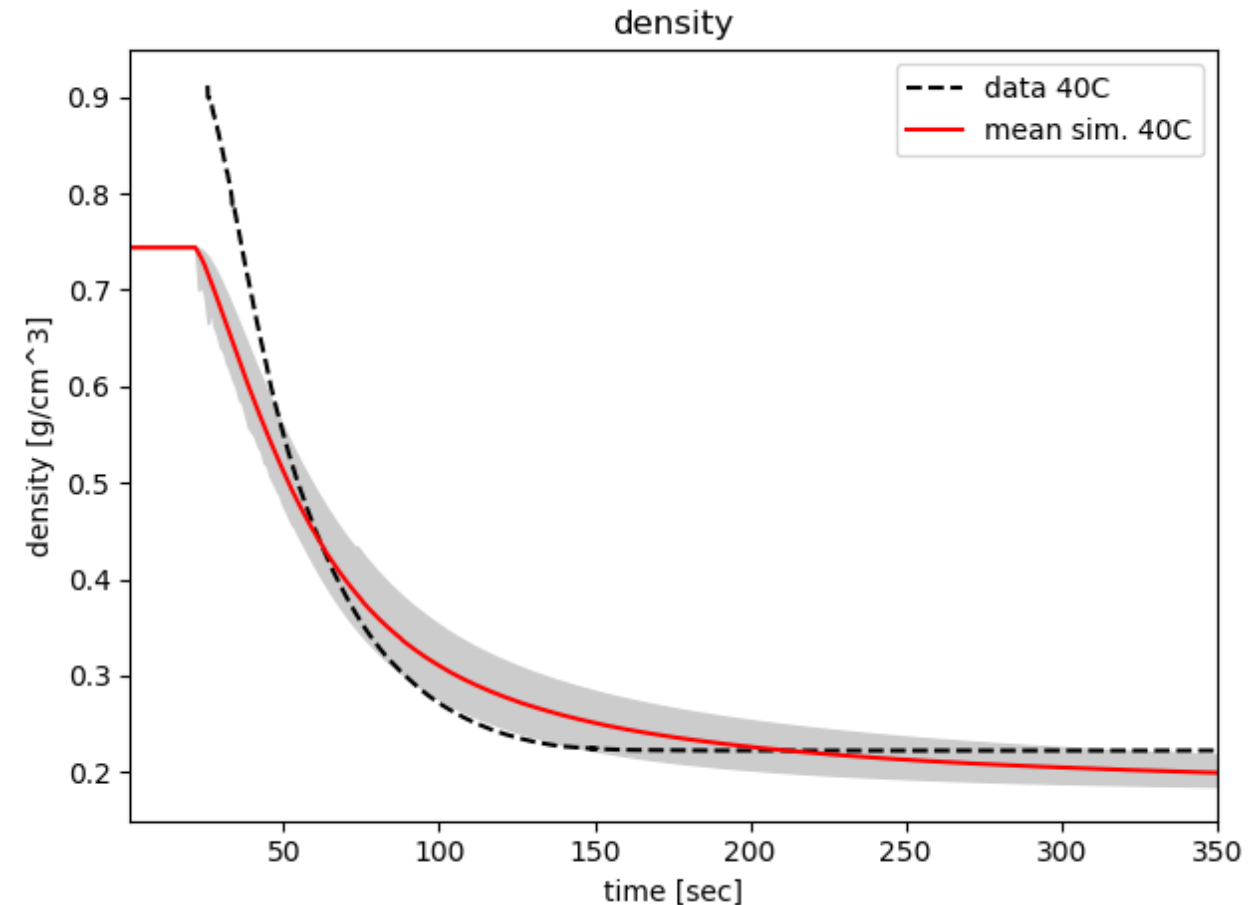
symbol	meaning
ρ	density
\mathbf{u}	mass-average fluid velocity
\mathbf{T}_f	stress tensor
f_Γ	surface tension
ξ	extent of reaction
k	rate constant
D_i	diffusion coefficient for variable i
b, m, n, p	fitting parameters
λ	thermal conductivity
T	temperature
Y	liquid mass fraction
H_{rxn}	heat of reaction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

Previous Work on PBE Modeling of Polyurethane Foam



- ⁴Karimi et al baseline population balance equation modeling for polyurethane foams
- ^{2,3}Rao et al developed a kinetics based model which tracked the curing reaction through extent of reaction
- ¹Ortiz et al added a population balance equation to Rao et al.'s model to track bubble size, which included coalescence and growth

We build on this work by adding both nucleation and breakage to the population balance equation



¹Ortiz, 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.

⁴Karimi, Mohsen, and Daniele L. Marchisio. "A baseline model for the simulation of polyurethane foams via the population balance equation" Macromolecular Theory and Sim. 2015.

Model PMDI-10 filling a 3D cylindrical mold



- Model a continuous liquid phase with a gaseous disperse phase (bubbles) which cures over time
- Phase space property: bubble volume, $\xi=v$

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

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

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:^{4,1}
$$\beta_p(v, v') = \beta_0(v + v')$$

Breakage kernel:⁷
$$a(v) = a_0 v^\alpha$$

Fragment distribution : ⁷
$$b(v|v') = \begin{cases} 2 & \text{if } v = \frac{v'}{2} \\ 0 & \text{else} \end{cases}$$

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



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

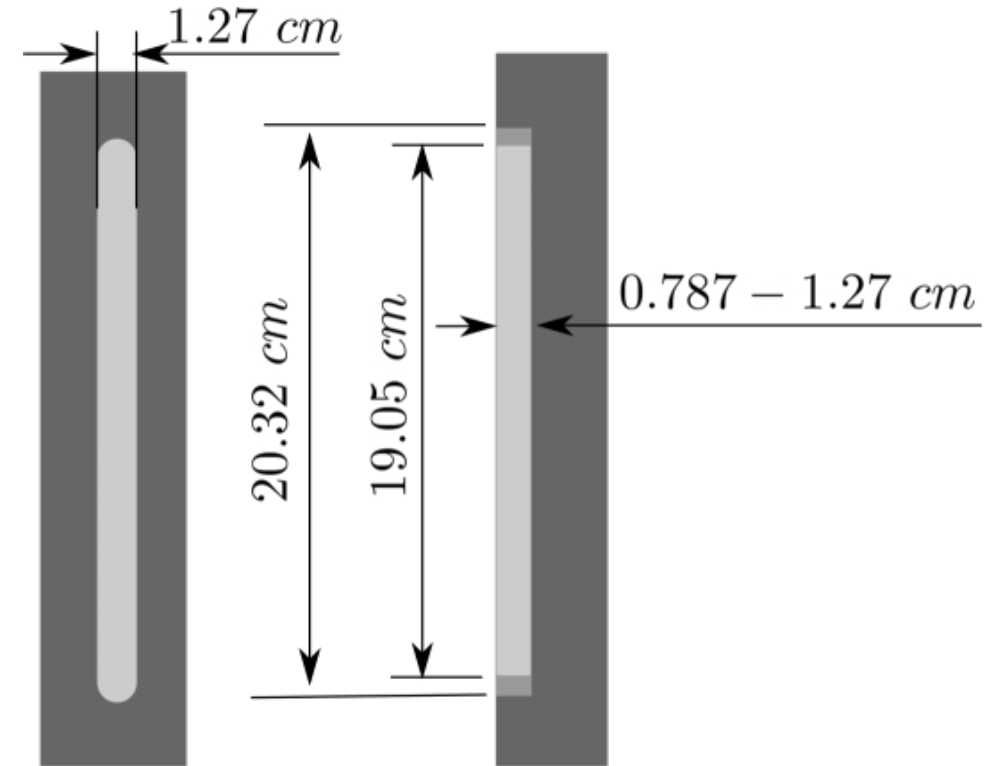
⁴Karimi, Mohsen, and Daniele L. Marchisio. "A baseline model for the simulation of polyurethane foams via the population balance equation" Macromolecular Theory and Sim. 2015.

⁷Marchisio, Daniele L., R. Dennis Vigil, and Rodney O. Fox. "Quadrature method of moments for aggregation-breakage processes." Journal of colloid and interface science. 2003.

Summary of Numerical Methods



- Implemented in the open-source software Goma
- Arbitrary Lagrangian-Eulerian
- Implicit Euler time integration (except moment source)
- PBE solved via quadrature method of moments (QMOM)
- Nodes and weights found using the Adaptive Wheeler Algorithm⁹
- For N -node quadrature we only need $2N$ moment
- Initialize moments assuming log-normal NDF



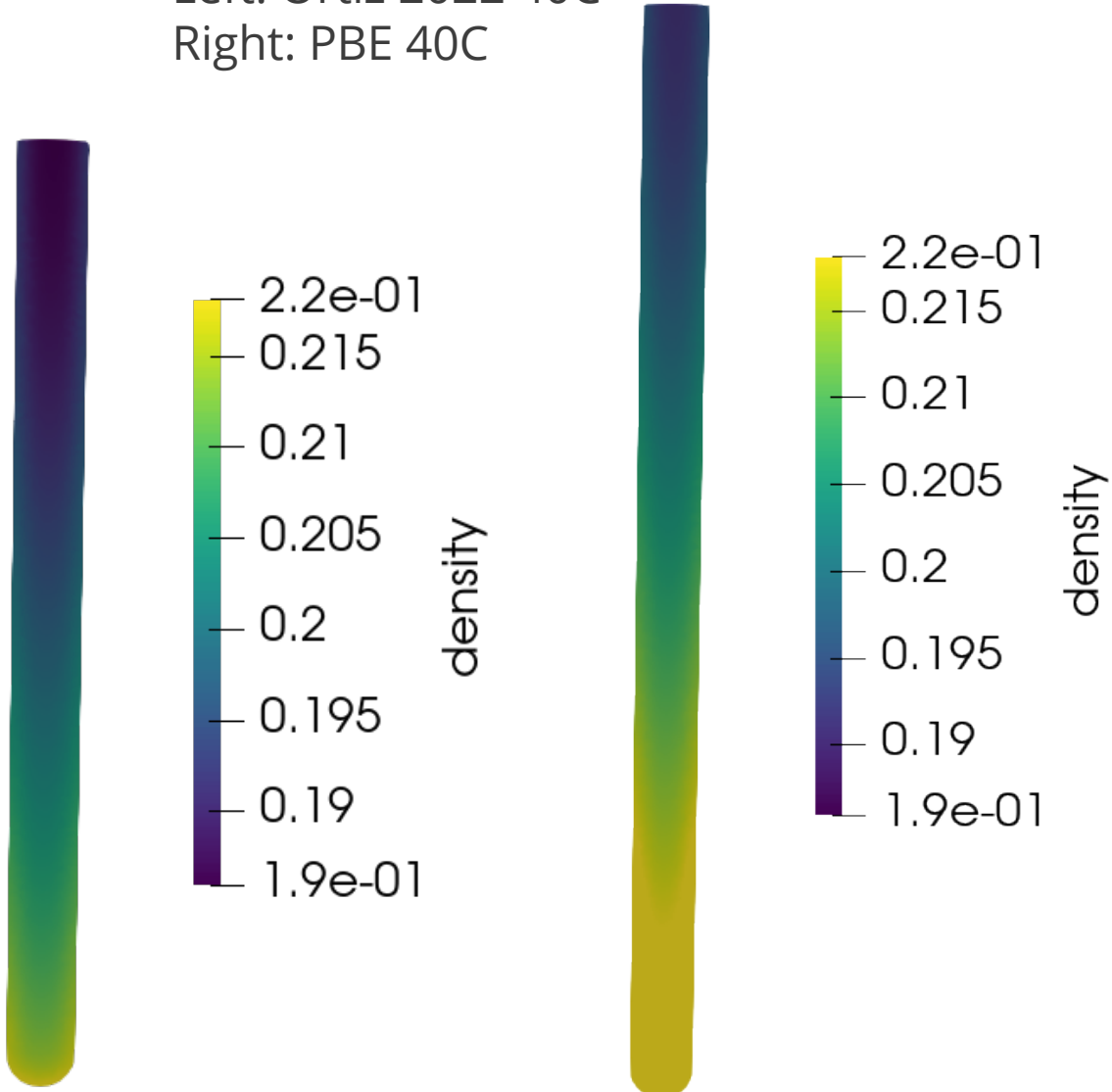
¹Ortiz, Weston, et al. "Population balance modeling of polyurethane foam formation with pressure- dependent growth kernel." *AIChE Journal*. 2022.

¹⁰Yuan, Cansheng, and Rodney O. Fox. "Conditional quadrature method of moments for kinetic equations." *Journal of Computational Physics*. 2011.

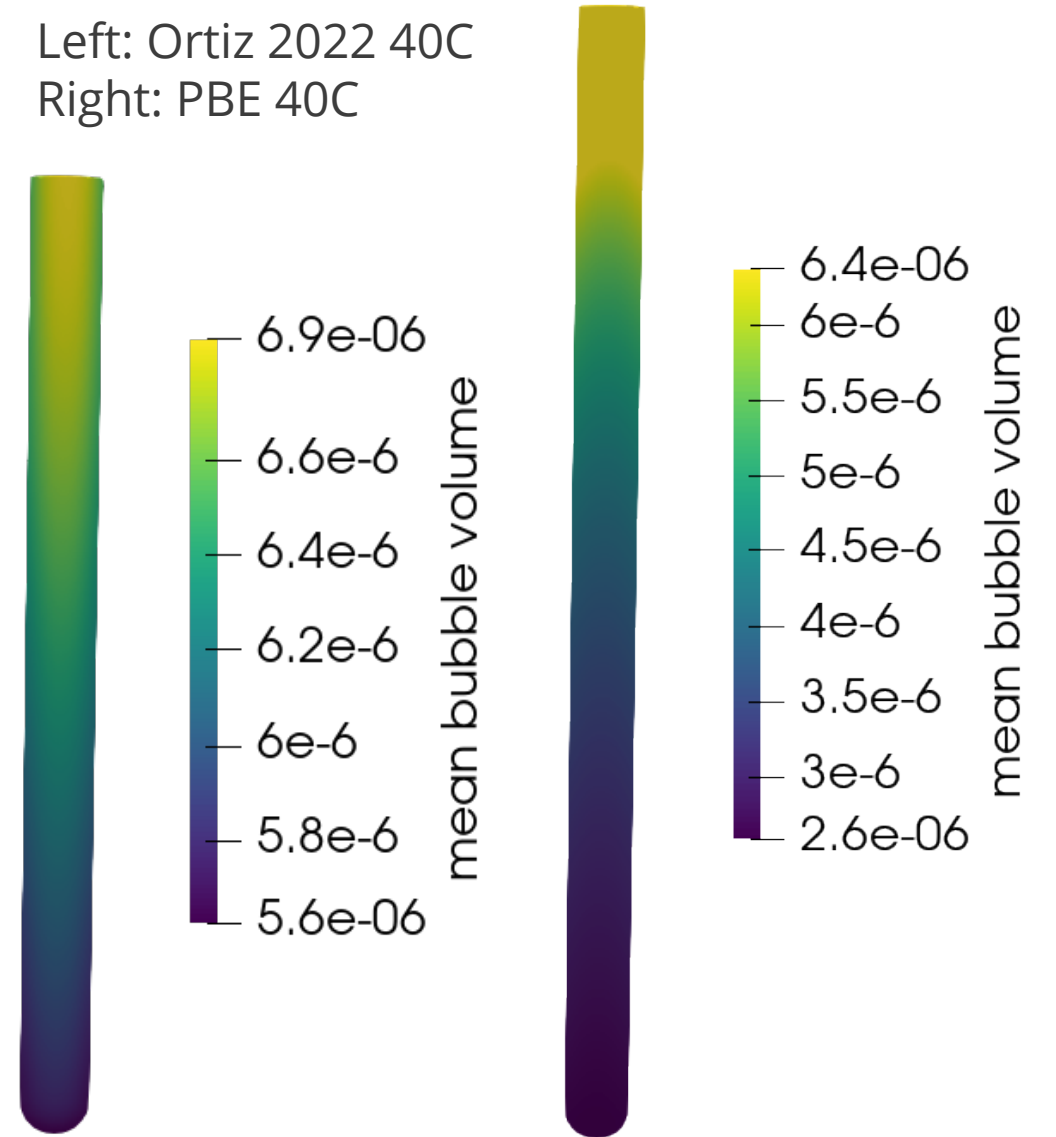
Results



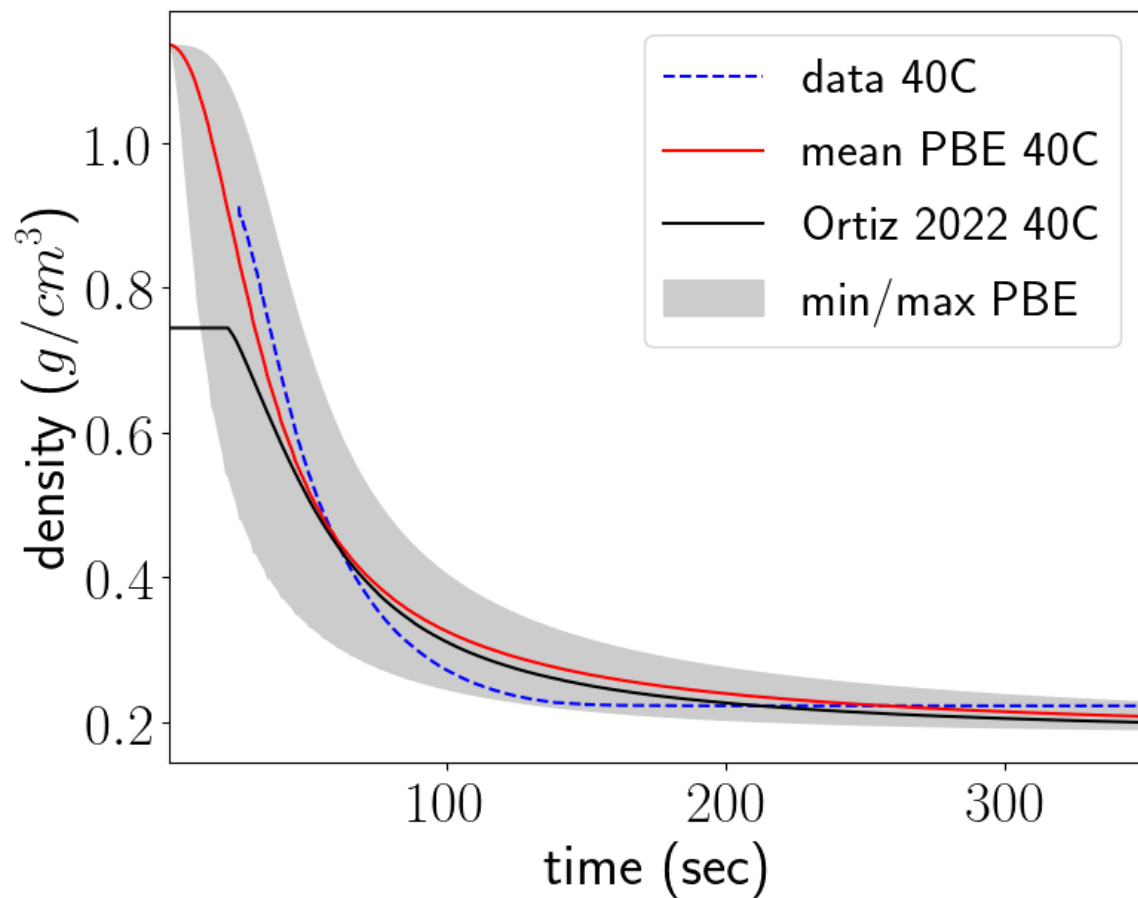
Left: Ortiz 2022 40C
Right: PBE 40C



Left: Ortiz 2022 40C
Right: PBE 40C



Results Continued

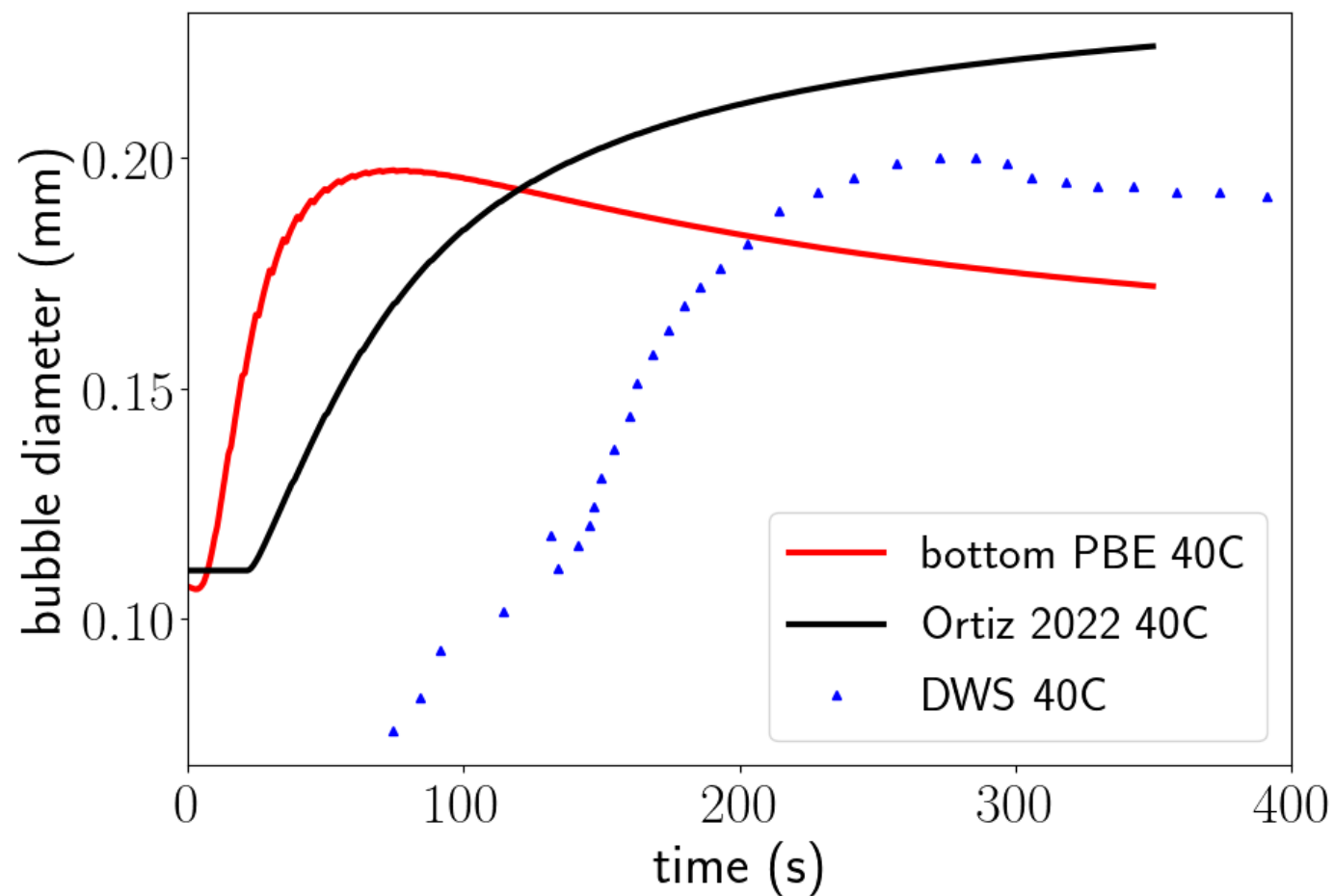


- Capturing early density well and producing similar shape to both data and Ortiz et al. 2022

Results Continued

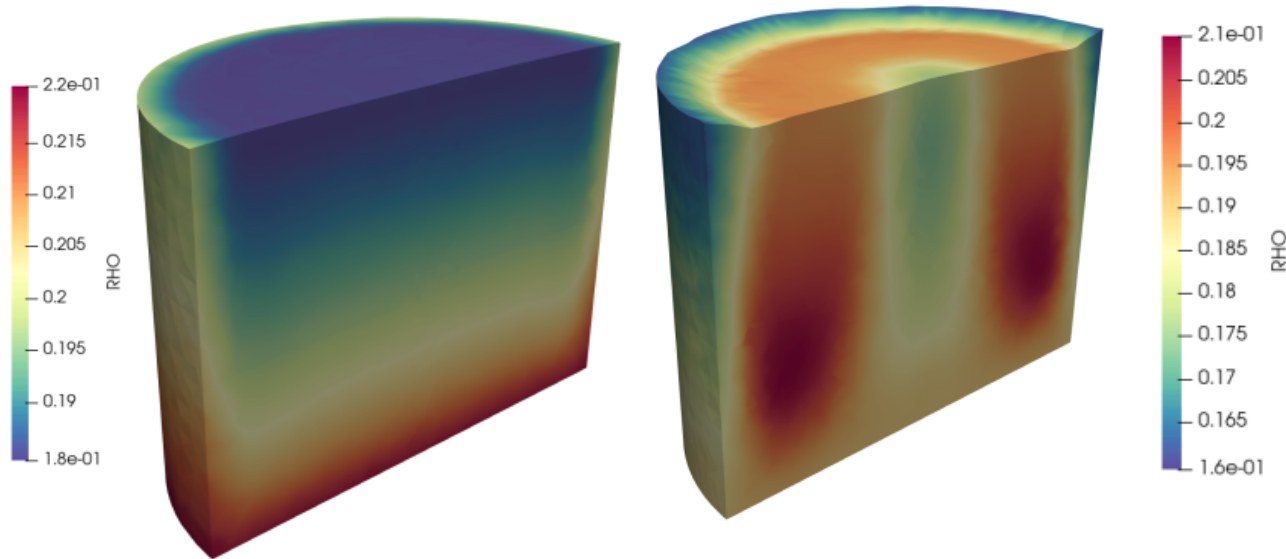


Bottom: 2.5cm from base of mold

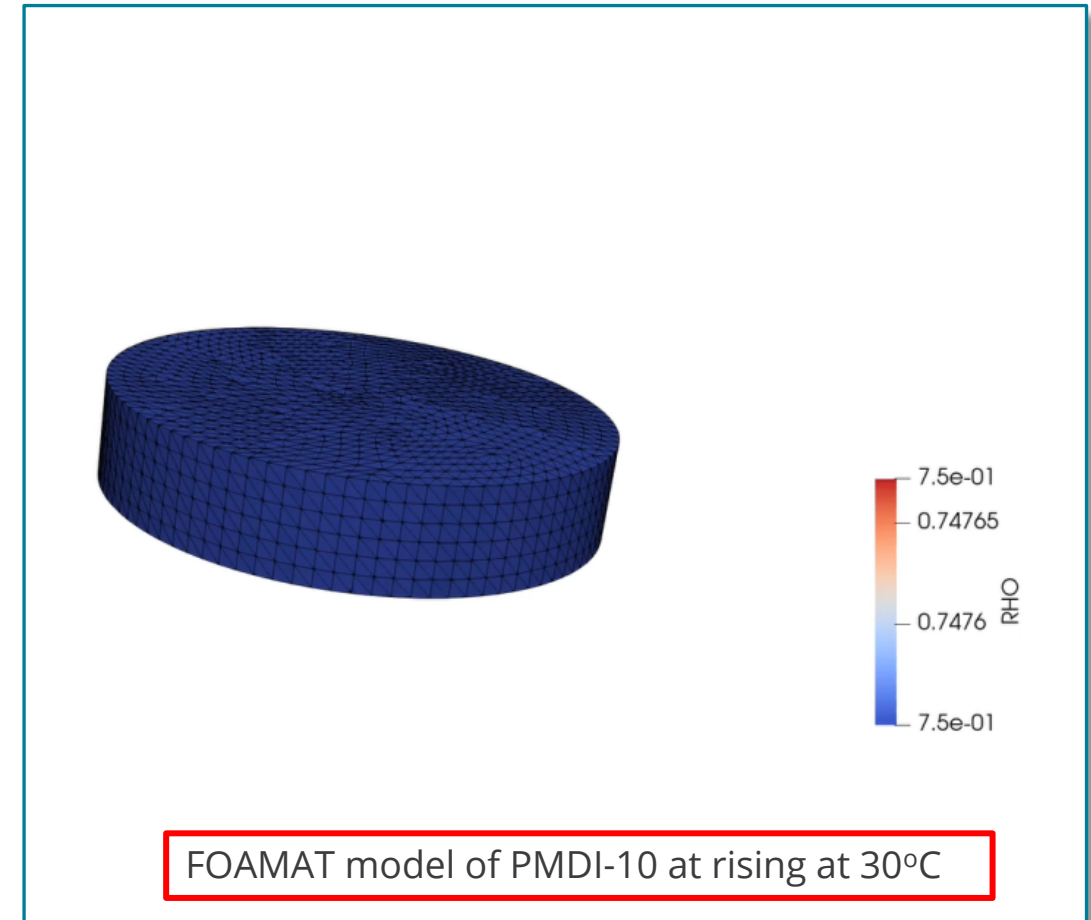


DWS: Diffusion Wave Spectroscopy

FOAMAT Results



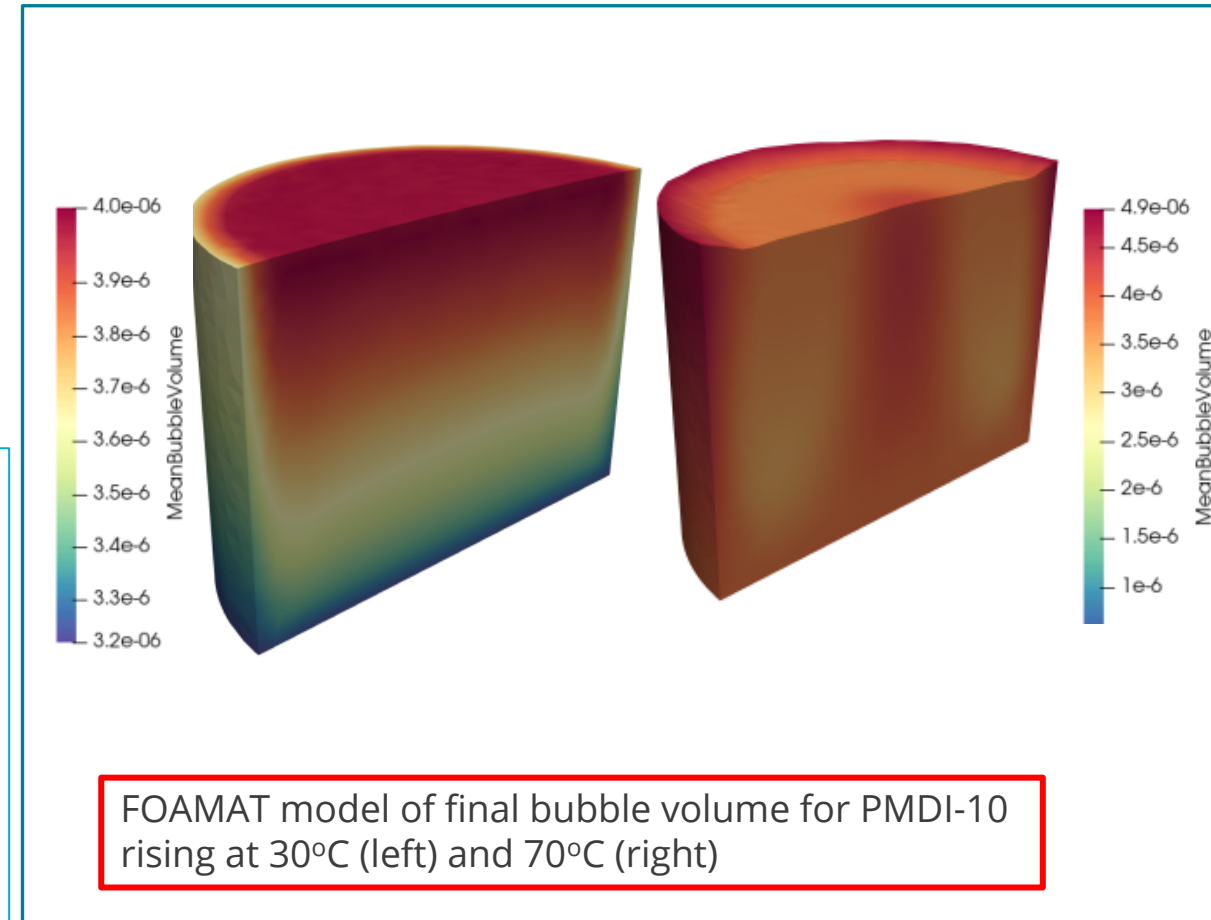
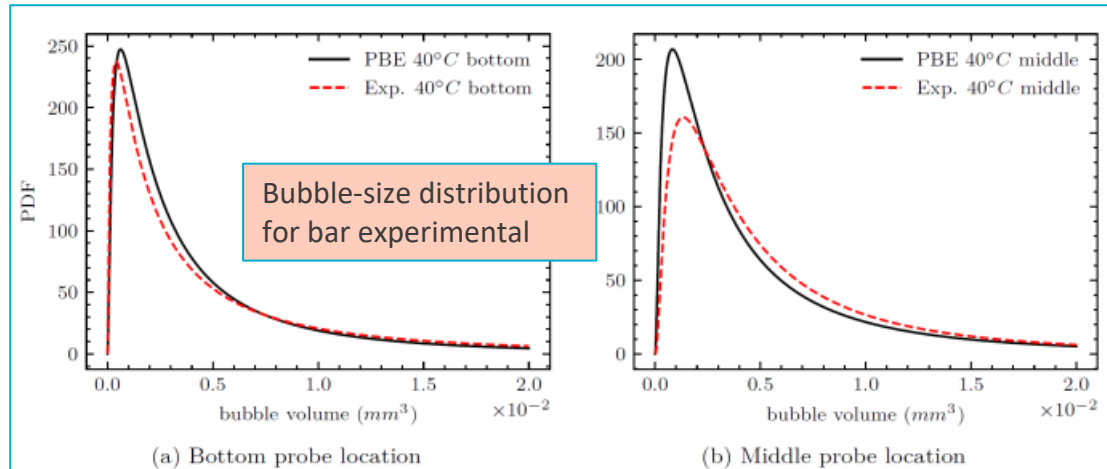
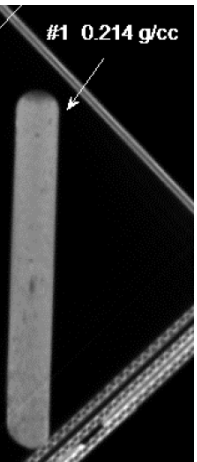
- FOAMAT used in industry to characterize the foam and compare formulations
- Model using 3D ALE with adaptive remeshing from the Omega-h library
- Test model on foaming for two different temperatures 30°C (left figure above) and 70°C (right figure above)



Model can be used to test different temperatures and the resulting foam density and bubble-size distribution

FOAMAT Results

- Moment equations predict average bubble size and bubble-size distribution at each node in the mesh
- On average, the bubbles are smaller in the hotter foam and the density is higher
- Density and bubble-size trend compared correctly to similar experimental systems; however, we could expect an even higher density for the 70°C foam

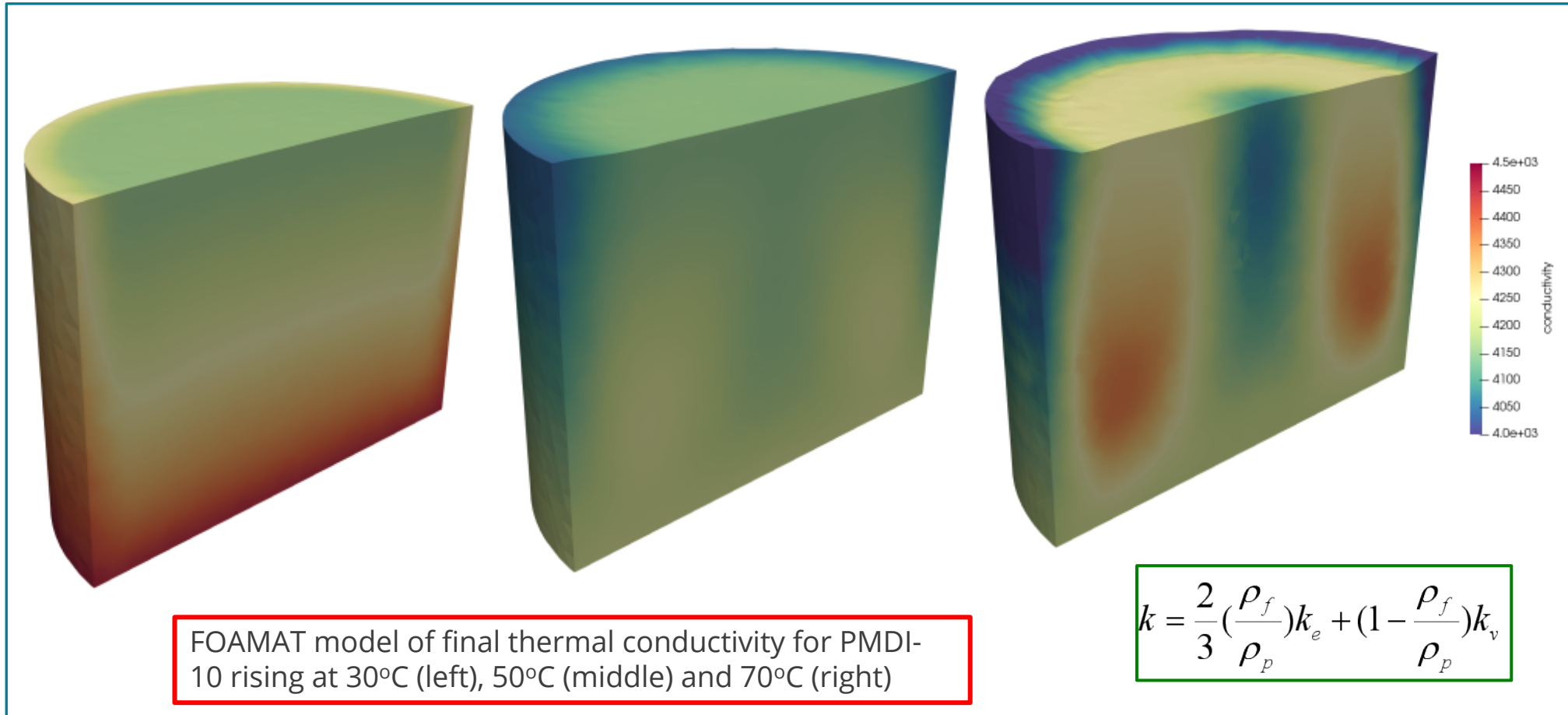


Model predicts variation in bubble-size distribution for 30°C versus 70°C

FOAMAT Results



- Thermal conductivity can be calculated from local density
- The more heterogenous the conductivity is the easier it is to lose heat and insulating factors
- Looking at correlations that include bubble-size as well as density



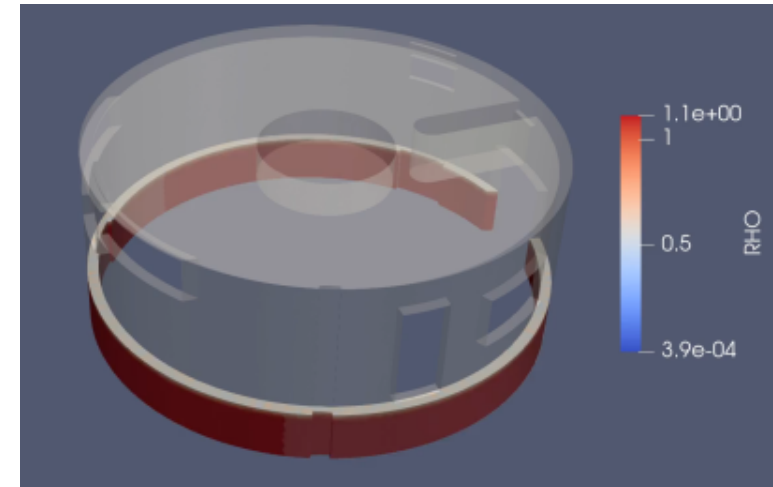
Thermal conductivity for 30°C, 50°C and 70°C

Summary:

- A coupled CFD-PBE approach has been developed for modeling polyurethane foam formation that can predict density, bubble-size distributions, and thermal conductivity for different processing conditions
- Numerical improvements underway for PBE in complex molds including level set
- Added nucleation and breakage 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 **emulsion data** for polymer upcycling
- Add small molecule crystallization to population balance including directional growth



Texts:

- ¹Ortiz, Weston, et al. "Population balance modeling of polyurethane foam formation with pressure- dependent growth kernel" AIChE Journal. 2022"
- ²Rao, Rekha, et al. "Density predictions using a finite element/level set model of polyurethane foam expansion and polymerization" Computers & Fluids 2018
- ³Rao, Rekha, et al. "The kinetics of polyurethane structural foam formation: Foaming and polymerization" AIChE Journal, 2017
- ⁴Karimi, Mohsen, and Daniele L. Marchisio. "A baseline model for the simulation of polyurethane foams via the population balance equation" Macromolecular Theory and Simulations
- ⁵Marchisio, Daniele L., and Rodney O. Fox. *Computational models for polydisperse particulate and multiphase systems*. Cambridge University Press, 2013
- ⁶Ramakrishna, Doraiswami. *Population balances: Theory and applications to particulate systems in engineering*. Elsevier, 2000
- ⁷Marchisio, Daniele L., R. Dennis Vigil, and Rodney O. Fox. "Quadrature method of moments for aggregation–breakage processes" Journal of colloid and interface science. 2003
- ⁸McGraw, Robert. "Description of aerosol dynamics by the quadrature method of moments" Aerosol Science and Technology. 1997.
- ⁹John 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
- ¹⁰Yuan, Cansheng, and Rodney O. Fox. "Conditional quadrature method of moments for kinetic equations" Journal of Computational Physics. 2011.
- ¹¹Mondy LA, Roberts CC, Soehnel G, et al. Bubble-size evolution during polyurethane foam expansion. Technical Report No SAND2016-5445. Office of Scientific and Technical Information (OSTI). 2016

Images/photos:

[US Korea Hotlink](#)

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

PU Vacuum Foaming Molds | Refrigerator Door, Cabinet

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.