

A Bubble-Scale Continuum Approach to Foam Expansion and Bubble Pressurization

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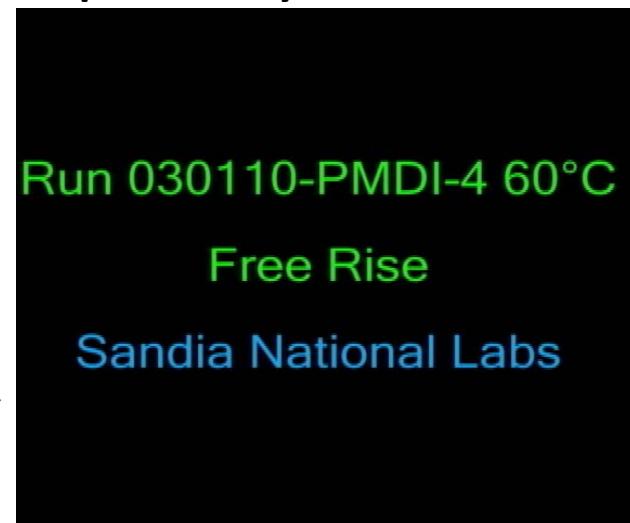


Cradle-to-Grave Model of PMDI Foam

Overarching Goal: A computational model for foaming, vitrification, cure, 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



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



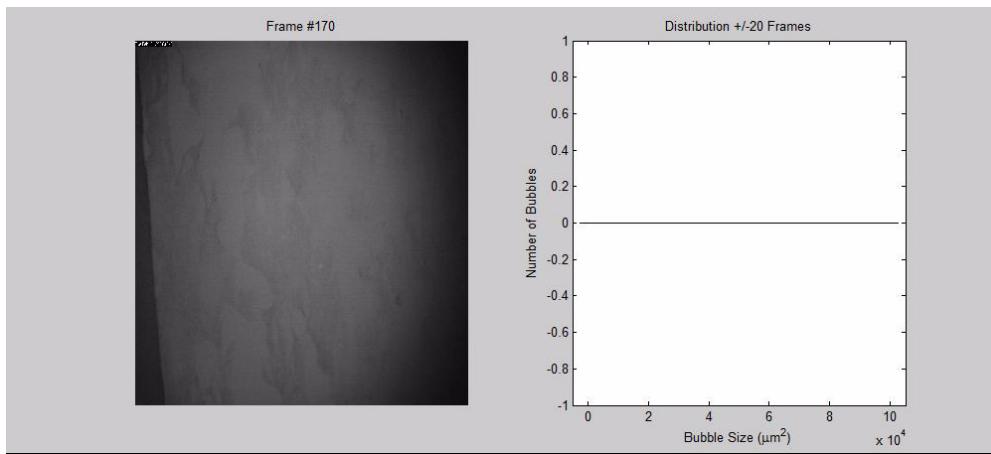
Remove
from mold –
predict cure
and thermal
stresses



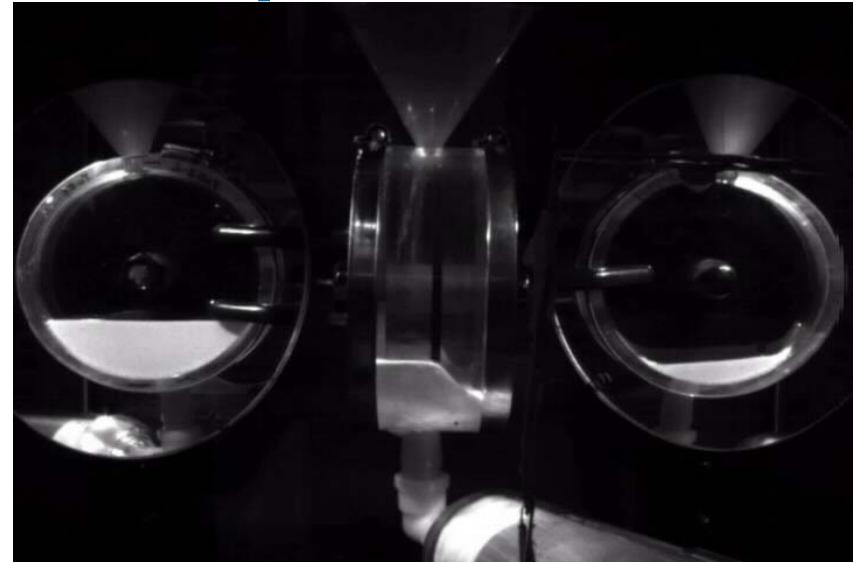
Predict
shape and
size over
years



Foam Filling is Complex



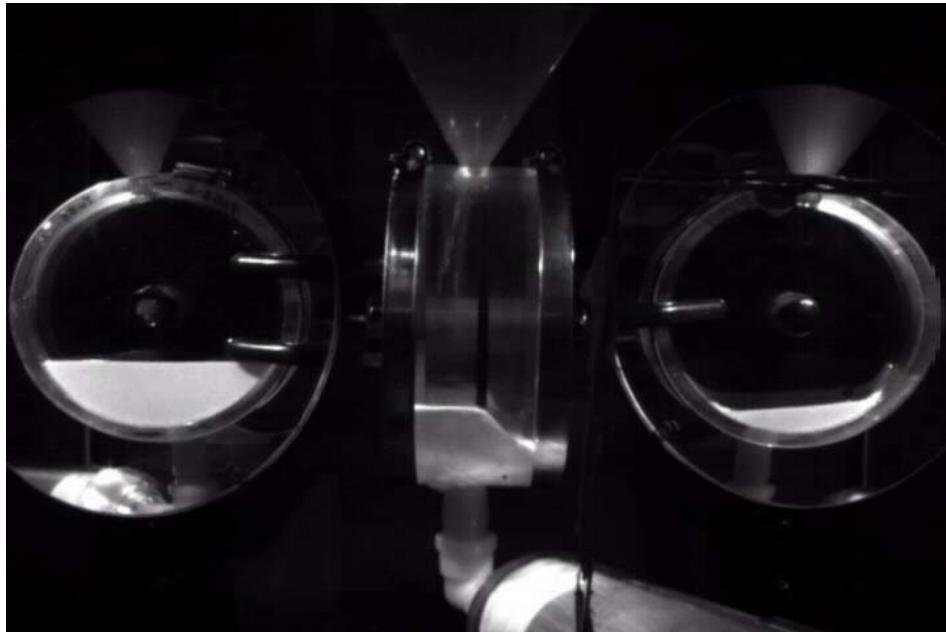
Foam front moving past camera, with bubble sizes at transparent wall determined with image processing.



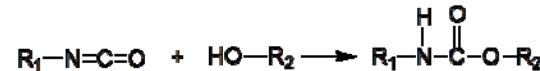
3 views of foam filling a mock AFS with several plates spaced unevenly. Vent location is critical to keep from trapping air.

- PMDI is used as an encapsulant for electronic components and lightweight structural parts, to mitigate against shock and vibration.
- **We would like to develop a computational model to help us understand foam expansion for manufacturing applications and how inhomogeneities effect the structural response of the final part, including long term shape stability.**
- 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.

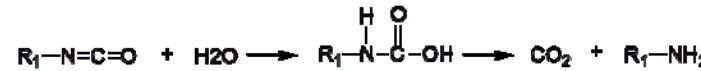
PMDI Foam Filling Simulation of Complex Part



Two key reactions: Isocyanate reaction with polyols and water



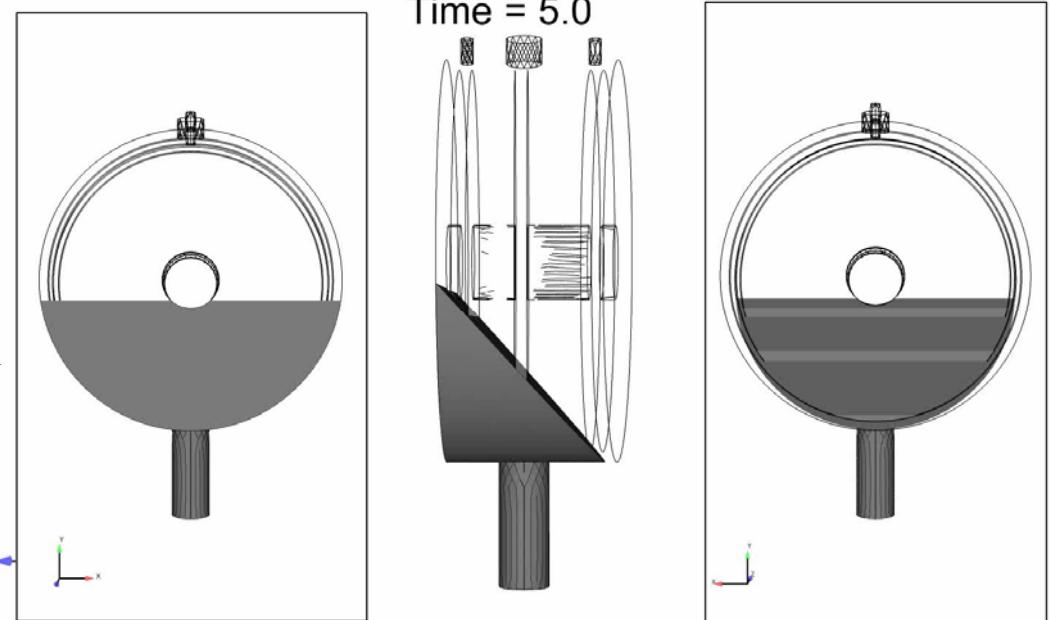
Urethane formation, crosslinking



Foaming reaction yields CO_2 and amine

Various follow up reactions: Isocyanate reaction with amine, urea and urethane

- Isocyanate reacts with water to create gas and foam expansion, changing the material from a viscous liquid to a multiphase material.
- Isocyanate reacts with polyol to polymerizes and vitrify to a solid.



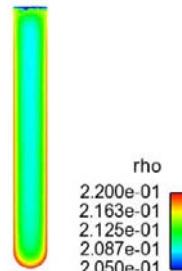
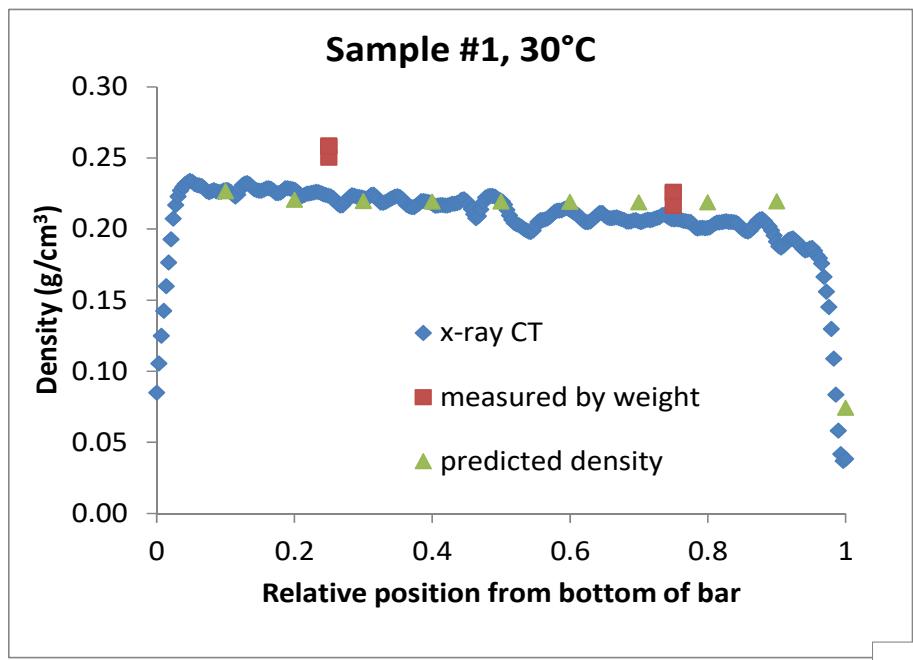
Coupled Finite Element Method/Level Set to Solve Foam Dynamics

- Gas and liquid are homogenized to a continuum
- Density evolves based on kinetics of gas expansion
- Viscosity evolves with cure and gas fraction

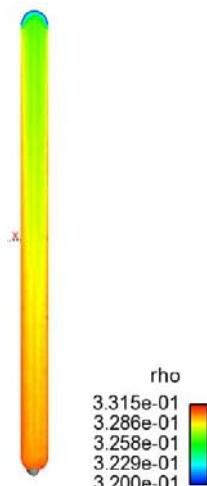
Rao et al., "Polyurethane kinetics for foaming and polymerization, *AIChE Journal*, 2017

Rao et al, "A Level Set Method to Study Foam Processing," *IJNMF*, 2012

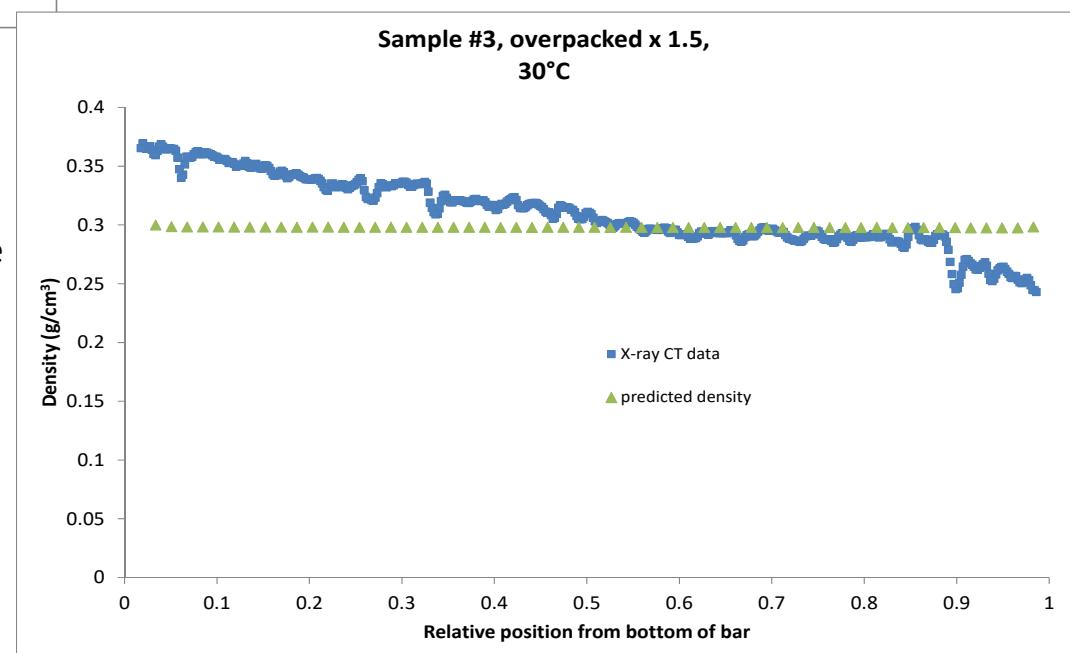
Density Study for Structural Foam PMDI-10



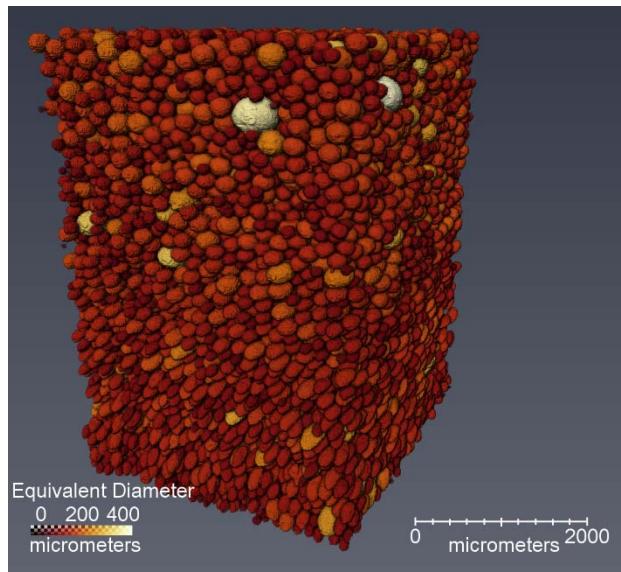
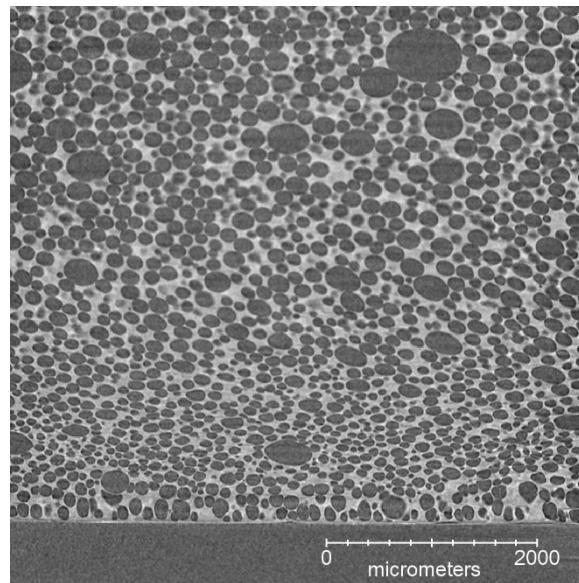
- Free rise foam density gradients. Plots are shown at the centerline of the foam cylinder
- Cylinder is under filled to give the free rise density



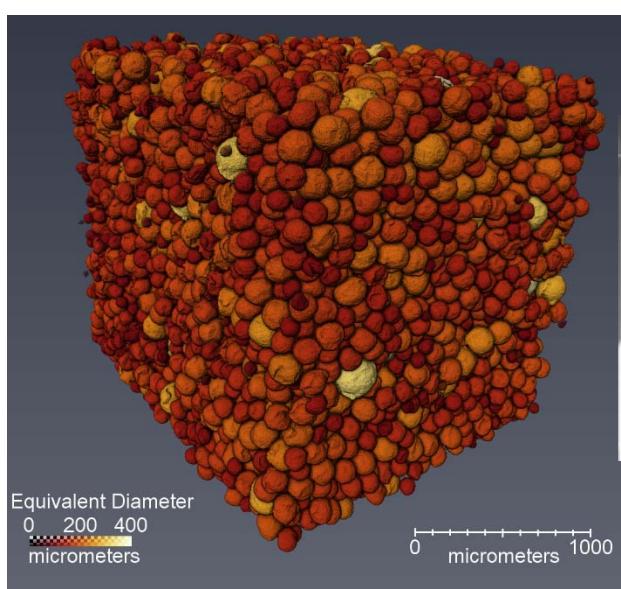
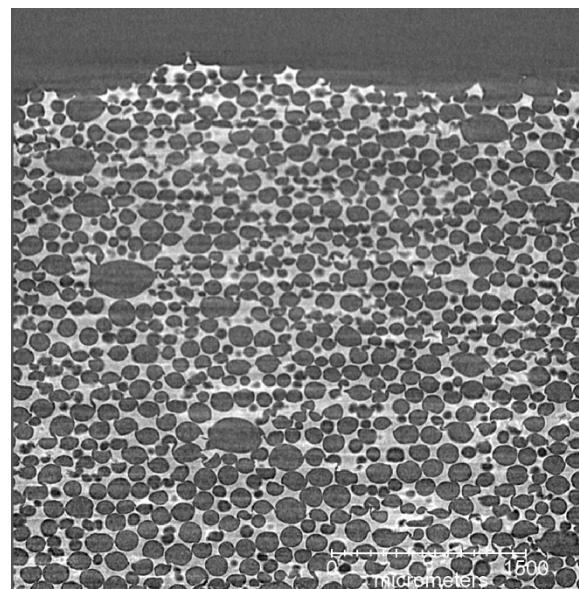
- Over packed (1.5) foam density gradients. Plots are shown at the centerline of the foam cylinder
- Self-closing vent lets air out, but keeps foam in for pressurization



CT Microstructure of Bubbles from Large Complex Mold



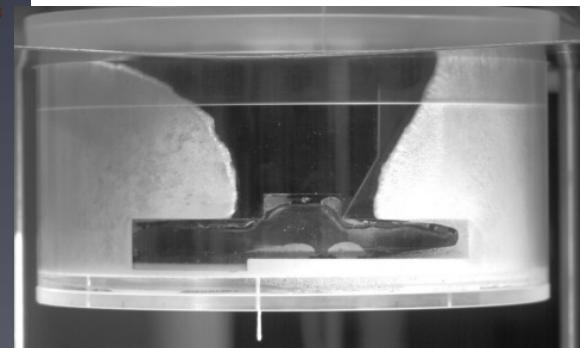
Sample 1 top



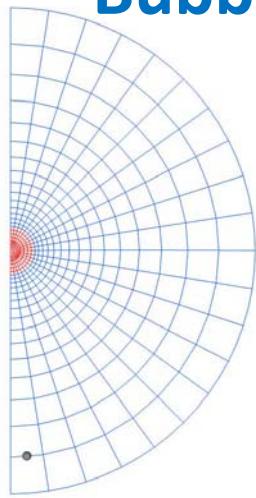
Sample 1 bottom

Foam microstructure

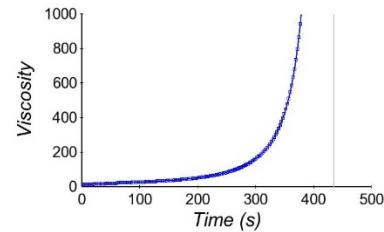
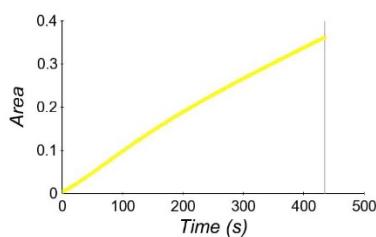
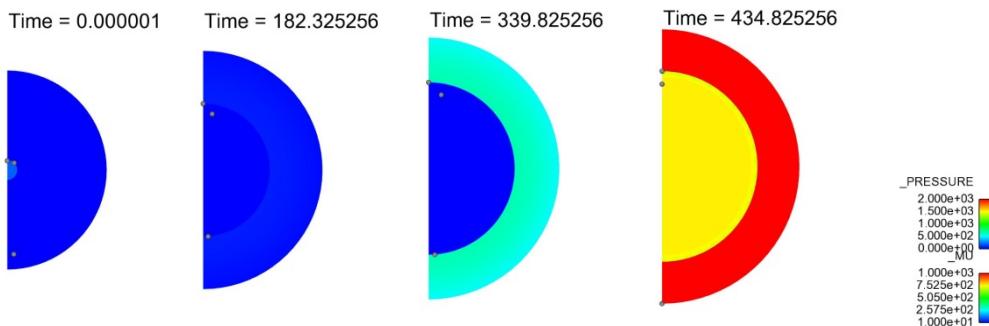
- Polydisperse bubble sizes
- Shear near boundaries cause elongated ellipsoidal bubbles



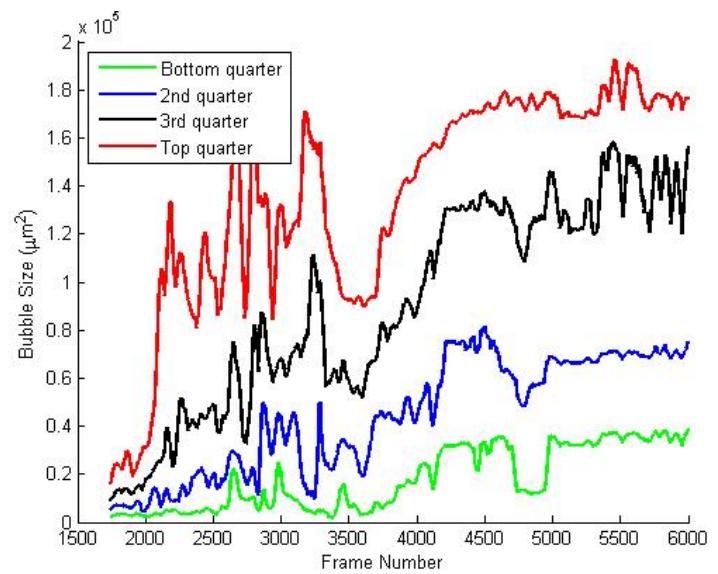
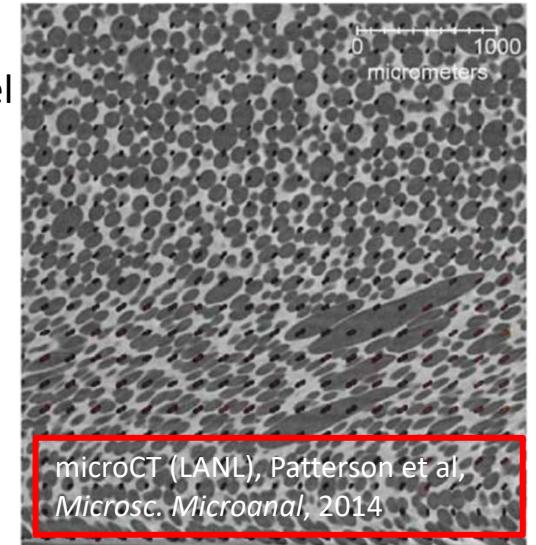
Bubble Expansion in a Polymerizing Fluid



- Bubble grows as CO_2 enters the bubble (VLE model)
- Growth is halted abruptly once the polymer reaches the gel point and the viscosity diverges
- Post-gelation, bubble pressurization is observed
- ALE mesh is robust over shape change
- Data shows the correct trends when compared to experiment



$$\rho \left(\frac{3}{2} \dot{R}^2 + \ddot{R} R \right) = p_{\text{gas}} - p_{\text{liq}} - 2 \frac{\sigma}{R} - 4 \eta_{\text{polymer}} \frac{\dot{R}}{R}$$



Equations of Motion Include Evolving Material Models

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

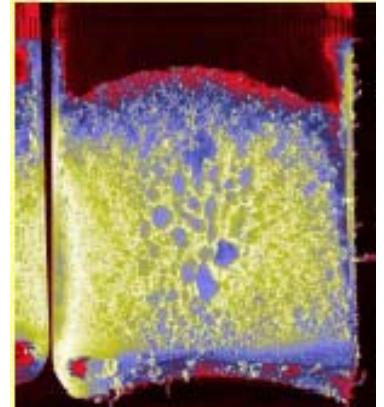
$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\rho \mathbf{v} \bullet \nabla \mathbf{v} - \nabla p + \nabla \bullet (\mu_f (\nabla \mathbf{v} + \nabla \mathbf{v}^t)) - \nabla \bullet \lambda (\nabla \bullet \mathbf{v}) \mathbf{I} + \rho \mathbf{g}$$
$$\frac{D \rho_f}{Dt} + \rho_f \nabla \bullet \mathbf{v} = 0$$

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

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

Extent of reaction equation for polymerization: condensation chemistry with T_g evolution

$$\frac{\partial \xi}{\partial t} = \left(\frac{1}{(1+wa)^\beta} \right) \left(k_0 \exp\left(-\frac{E}{RT}\right) \right) (b + \xi^m) (1 - \xi)^n \quad \log_{10} a = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \quad T_g = \frac{T_{g0}(1 - \xi) + A\xi T_{g\infty}}{(1 - \xi + A\xi)}$$



NMR imaging shows coarse microstructure (Altobelli, 2006)

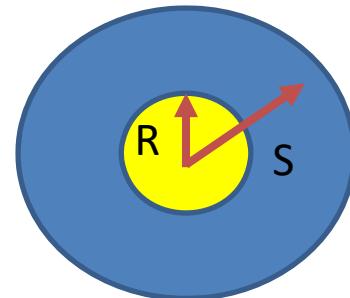
New molar concentration equations for water and carbon dioxide on the next page:
kinetics stay the same

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

Influence Volume Approach (IVA)

Interchange between bubbles and liquid phase occurs at interface

$$S_{pg} = 3 \frac{\varphi}{R} D_g \frac{\partial C}{\partial R} \Big|_{r=R} \quad R_{av} = \left[\frac{3}{4\pi} \frac{\varphi}{n} \right]^{1/3}, \quad S_{av} = \left[\frac{3}{4\pi} \frac{1}{n} \right]^{1/3}$$



IVA approach assumes a linear profile of CO₂ in the fluid (blue):

$$\frac{\partial C}{\partial R} \Big|_{r=R} = \frac{C_{CO_2} - C(R)}{\Delta r}, \quad C(R) = K_H p_{gas} \quad p_{gas} = \rho_{gas} \mathfrak{R} T / M_{CO_2}$$

$$S_{pg} = 3 \frac{\varphi}{R_{av}} D_g \frac{C_{CO_2} - K_H p_{gas}}{\Delta r}$$

$$\Delta r = \frac{(S_{av}^4 - R_{av}^4) - R_{av}(S_{av}^3 - R_{av}^3)}{S_{av}^3 - R_{av}^3}$$

Advection of Number Density Equation:

- We can either solve an advection equation (more accurate and expensive) or

$$\frac{\partial n}{\partial t} = \nabla \cdot (\vec{v} n)$$

Nomenclature

- n = nucleation sites/total volume (the number, N , is constant but the density changes over time (#/cc))
- m_{in} = initial mass injected (g)
- K_H = Henry's law coefficient

Newer Foam Expansion: Two-phase Carbon Dioxide Models

Water balance in the liquid phase (mol H₂O/volume total):

$$\frac{\partial C_{H_2O}}{\partial t} + \nabla \cdot \vec{v} C_{H_2O} = D_{H_2O} \nabla^2 C_{H_2O} - (1 - \varphi) k_{H_2O} C_{H_2O}^n$$

Carbon dioxide balance in the liquid phase (mol CO₂/volume total):

$$\frac{\partial C_{CO_2}}{\partial t} + \nabla \cdot \vec{v} C_{CO_2} = D_{CO_2} \nabla^2 C_{CO_2} + (1 - \varphi) k_{H_2O} C_{H_2O}^n - S_{pg}$$

Bubble conservation equation: it advects

Carbon dioxide balance in the gas phase (mol CO₂/volume total):

$$\frac{\partial C_{CO_2}^g}{\partial t} + \nabla \cdot \vec{v} C_{CO_2}^g = S_{pg}$$

$$S_v = \frac{3}{R} \dot{R} \approx \frac{1}{4\eta_{polymer}} ((p_{gas} - p_{liq}) - \frac{2\sigma}{R_{av}})$$

$$S_v = \frac{1}{4\eta_{polymer}} ((\rho_{gas} \mathfrak{R} T / M_{CO_2} - p_{liq}) - \frac{2\sigma}{R_{av}})$$

Carbon dioxide balance in the gas phase (mass CO₂/volume bubbles):

$$\frac{\partial \rho_{gas}}{\partial t} + \vec{v} \cdot \nabla \rho_{gas} = -\rho_{gas} S_v + M_{CO_2} S_{pg}$$

This term couples to the subscale. It is the added volume from the bubble size increase during a time step. S_v has unit of continuity. S_{pg} is the added mass from reactions.

Newer Foam Expansion: Two-phase Carbon Dioxide models

Continuity equation is foam density balance (g total/volume foam):

$$\frac{\partial \rho_f}{\partial t} + \vec{v} \cdot \nabla \rho_f + \rho_f \nabla \cdot \vec{v} = 0$$

Gas Volume Fraction (volume foam/volume total):

$$\phi(t) = \frac{\rho_{foam} Y_g}{\rho_{gas}} = \frac{M_{CO_2} C_{CO_2}^g}{\rho_{gas}}$$

Foam Density relationship is the same as before:

$$\rho_f = (\rho_{gas} - \rho_{liq})\phi(t) + \rho_{liq}$$

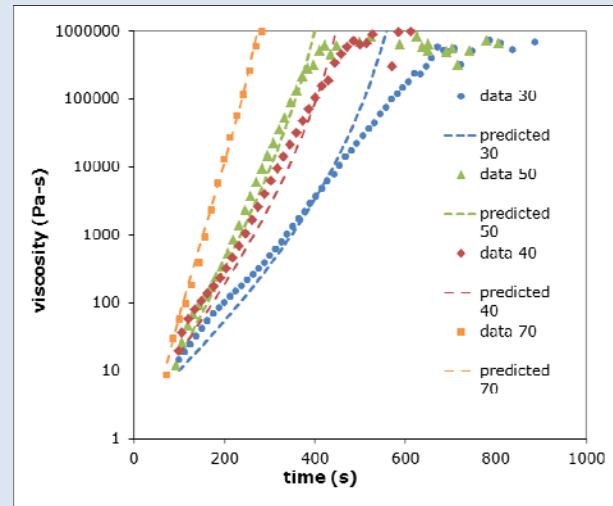
Model Foam Viscosity as $f(\xi, \phi)$

Start with continuous phase viscosity only

- IR kinetics + dry formulation rheology (two sets of experiments) give an approximation of the curing continuous phase rheology
- Relate time of gel point to ξ to find ξ_c .

$$\mu_{polymer} = \mu_0^0 \left(\frac{\xi_c - \xi}{\xi_c} \right)^{-6} \quad \xi_c = 0.86$$

$$\mu_0^0 = 600 e^{-1549/RT} \text{ Pa-s}$$

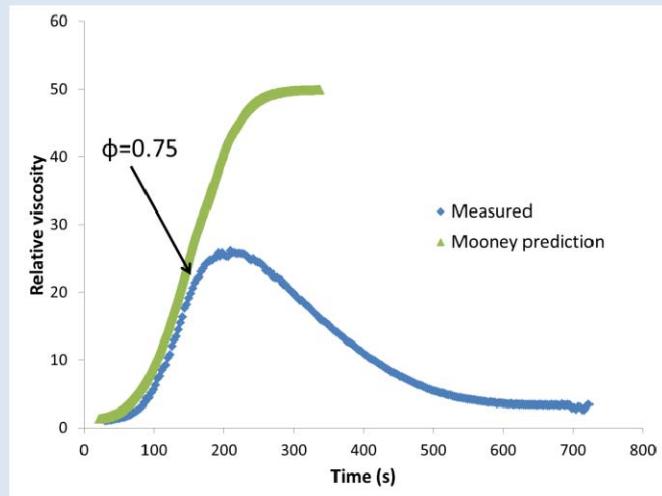


Relate foam viscosity to continuous phase viscosity

- Foam rise + wet formulation rheology (two sets of experiments) give an approximation of the rheology as a function of gas fraction
- Mooney prediction (for $\phi_{gas} < 0.5$)

$$\mu_\phi = \mu_{polymer} \exp \left(\frac{\phi_g}{1 - \phi_g} \right)$$

- For $\phi_{gas} > 0.75$ estimate $\mu_{foam} = \mu_{cure} * f(\xi)$



Including Bubble-Scale Effects

$$\frac{\partial C_{H_2O}}{\partial t} + \nabla \cdot \vec{v} C_{H_2O} = D_{H_2O} \nabla^2 C_{H_2O} - (1 - \varphi) k_{H_2O} C_{H_2O}^n \quad \text{Existing equation with minor mods}$$

$$\frac{\partial C_{CO_2}}{\partial t} + \nabla \cdot \vec{v} C_{CO_2} = D_{CO_2} \nabla^2 C_{CO_2} + (1 - \varphi) k_{H_2O} C_{H_2O}^n - S_{pg} \quad \text{Existing equation with mods including source}$$

$$\frac{\partial C_{CO_2}^g}{\partial t} + \nabla \cdot \vec{v} C_{CO_2}^g = S_{pg} \quad \text{New equation similar to liquid}$$

$$\frac{\partial \rho_{gas}}{\partial t} + \vec{v} \cdot \nabla \rho_{gas} = -\rho_{gas} S_v + M_{CO_2} S_{pg} \quad \text{New equation for bubble gas density}$$

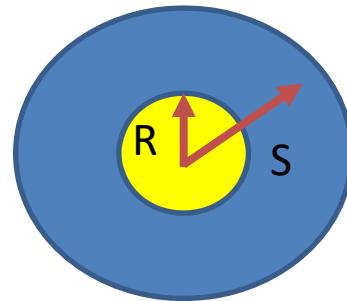
$$\frac{\partial n}{\partial t} = \nabla \cdot (\vec{v} n) \quad \text{New equation for bubble number density}$$

$$\varphi(t) = \frac{\rho_{foam} Y_g}{\rho_{gas}} = \frac{M_{CO_2} C_{CO_2}^g}{\rho_{gas}} \quad \rho_f = (\rho_{gas} - \rho_{liq}) \varphi(t) + \rho_{liq}$$

Source terms from bubble scale:

$$S_v = \frac{1}{4\eta_{polymer}} \left((\rho_{gas} \Re T / M_{CO_2} - p) - \frac{2\sigma}{R_{av}} \right)$$

$$S_{pg} = 3 \frac{\varphi}{R_{av}} D_{CO_2} \frac{C_{CO_2} - K_H \rho_{gas} \Re T / M_{CO_2}}{\Delta r}$$



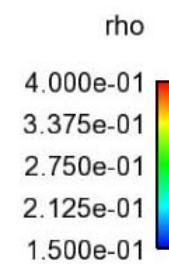
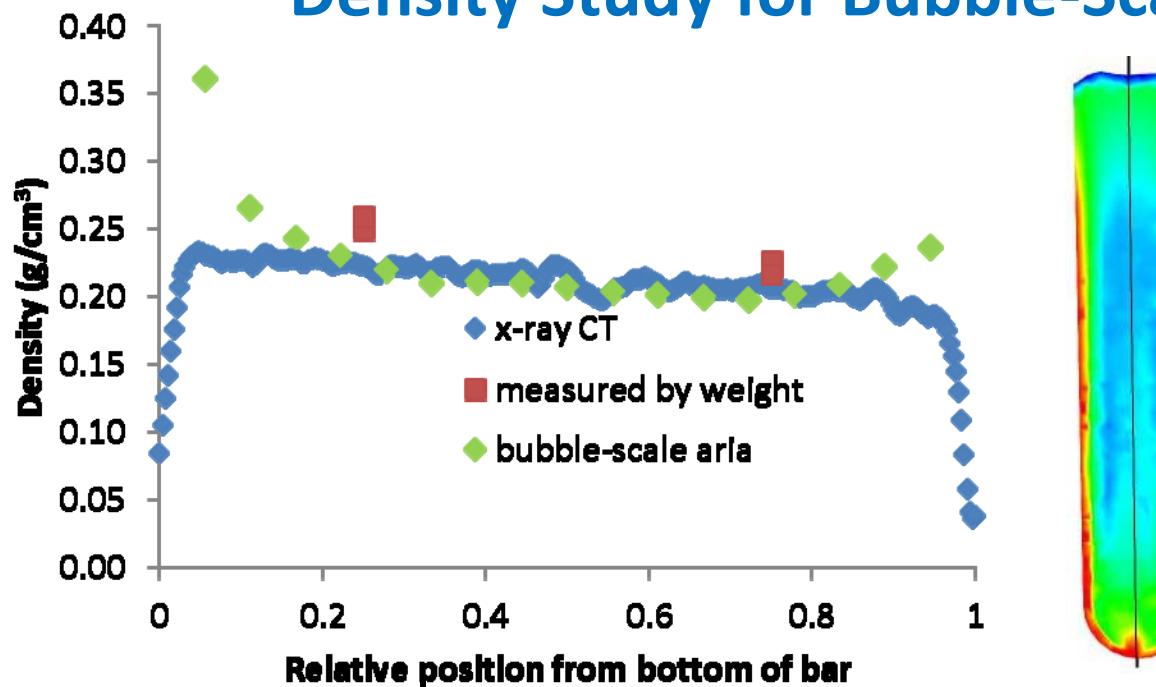
Influence volume approach

$$R_{av} = \left[\frac{3}{4\pi} \frac{\varphi}{n} \right]^{1/3}, \quad S_{av} = \left[\frac{3}{4\pi} \frac{1}{n} \right]^{1/3}$$

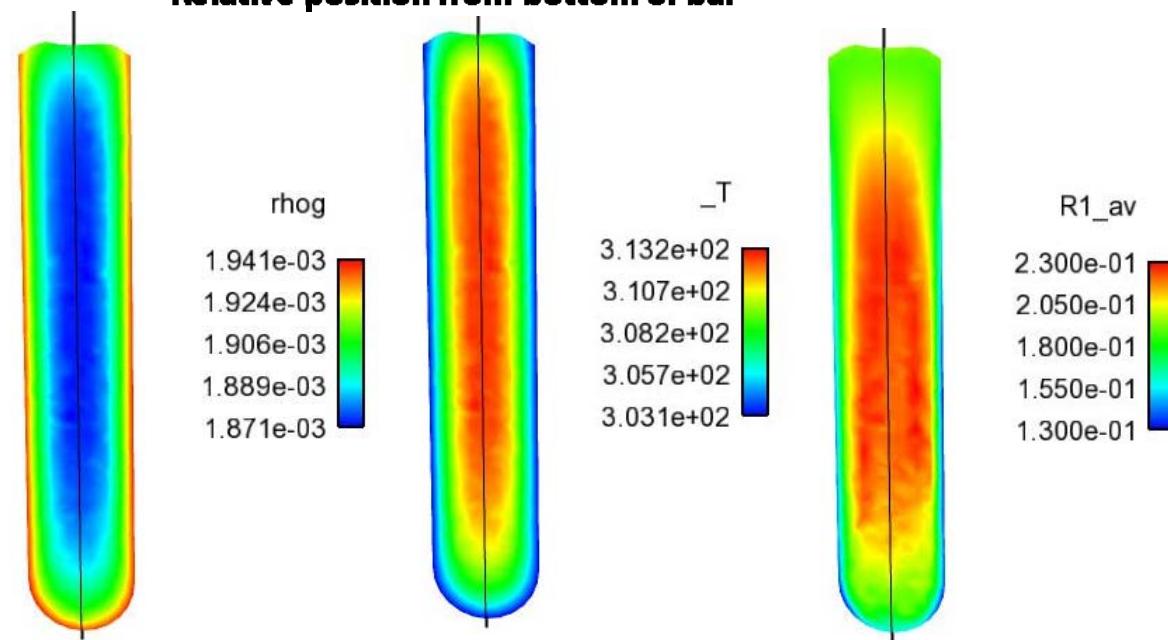
$$\Delta r = \frac{(S_{av}^4 - R_{av}^4) - R_{av}(S_{av}^3 - R_{av}^3)}{S_{av}^3 - R_{av}^3}$$

$$\eta_{polymer} = \eta_0^0 \exp\left(\frac{E_\mu}{RT}\right) \left(\frac{\xi_c^p - \xi^p}{\xi_c^p}\right)^{-q}$$

Density Study for Bubble-Scale Model

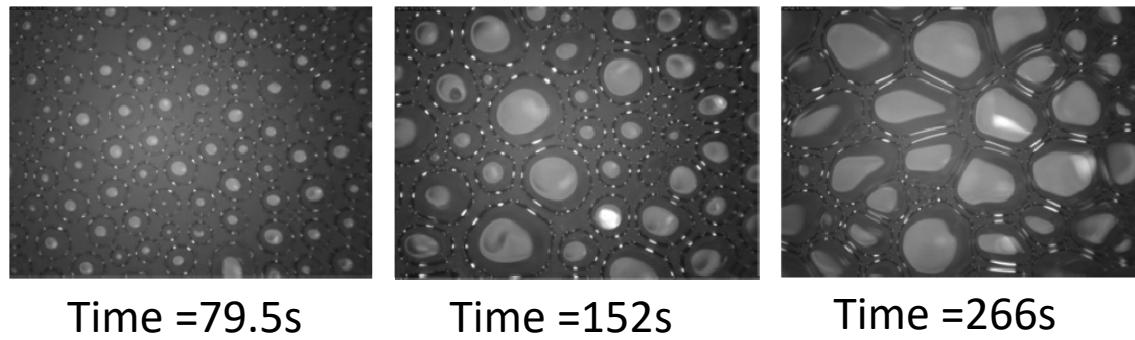


- Free rise foam density gradients. Plots are shown at the centerline of the foam cylinder



Density Study for Bubble-Scale Model

PMDI-4 free rise (bottom camera)

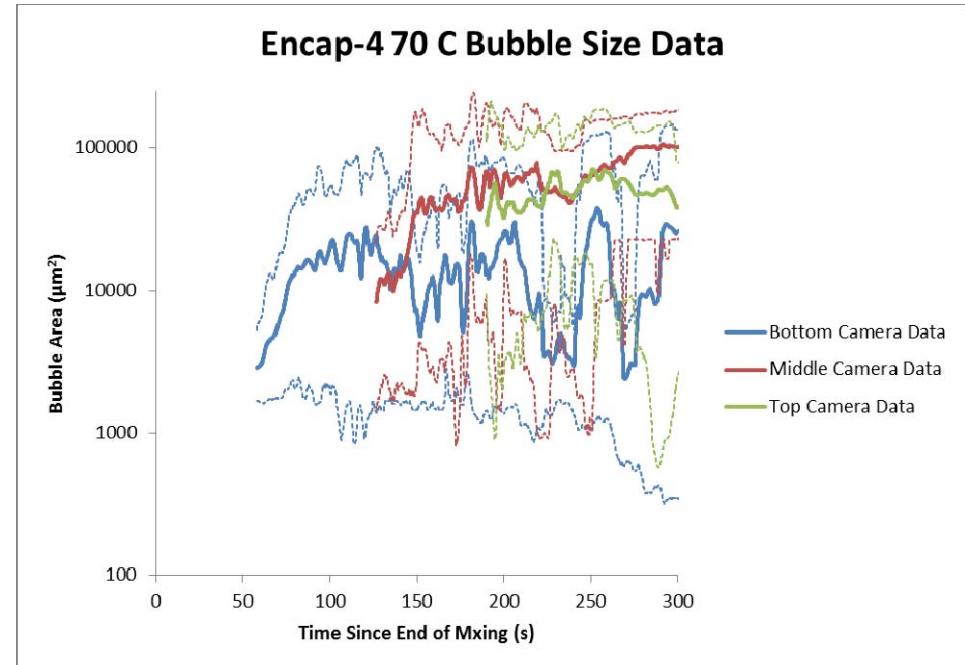
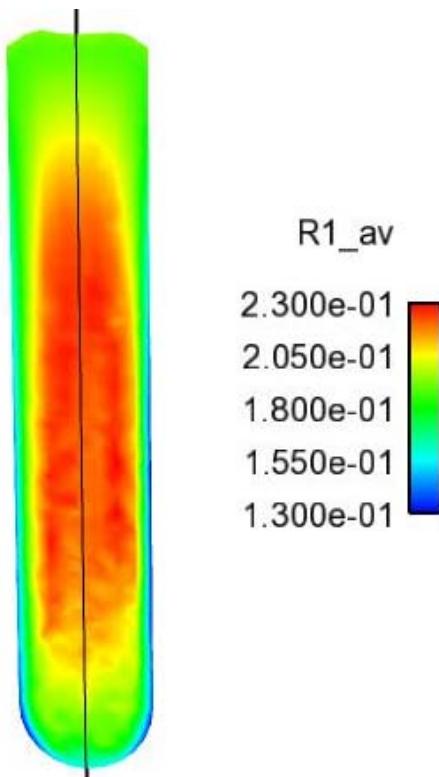


Time = 79.5s

Time = 152s

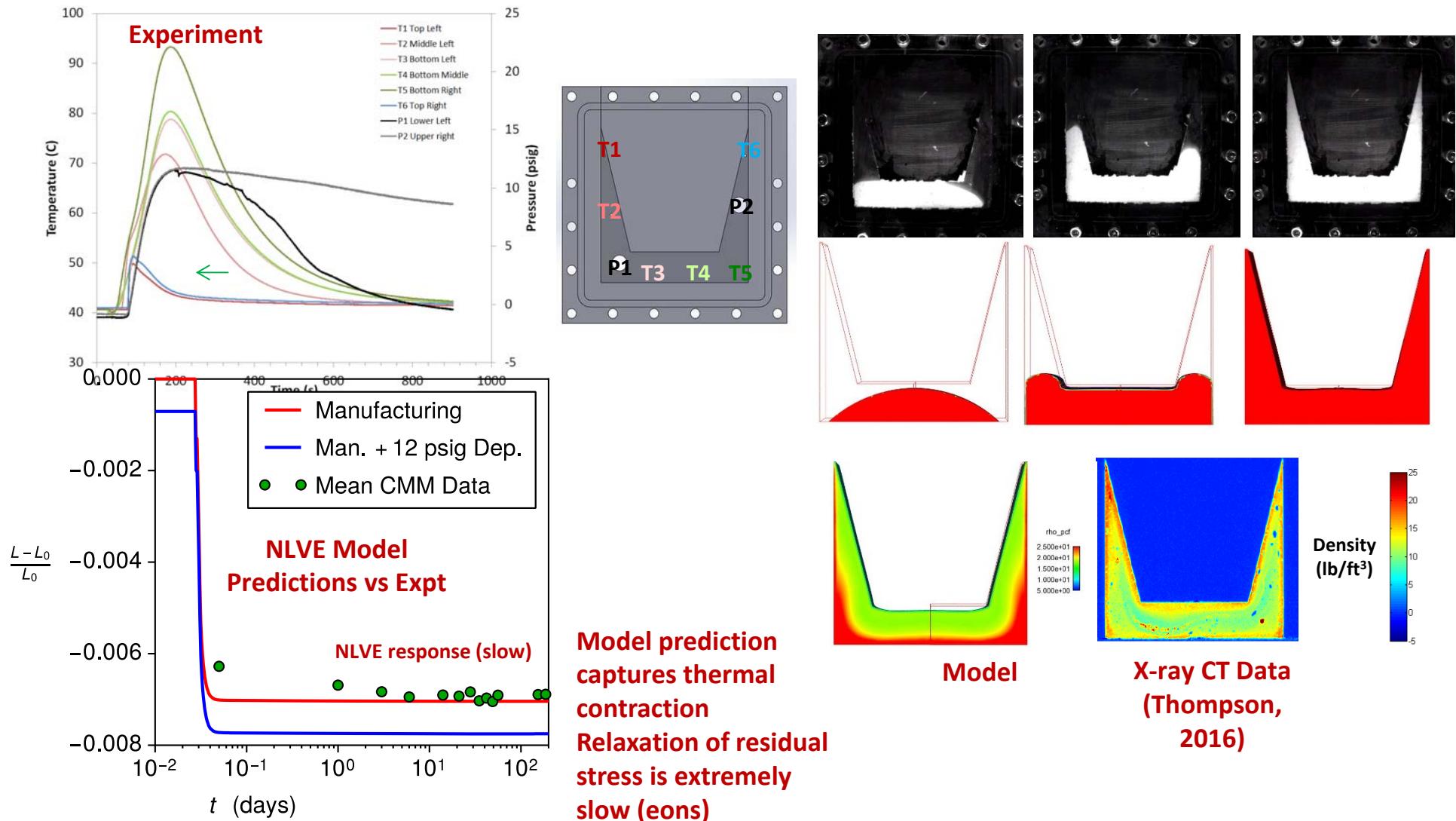
Time = 266s

- Free rise foam density gradients. Plots are shown at the centerline of the foam cylinder



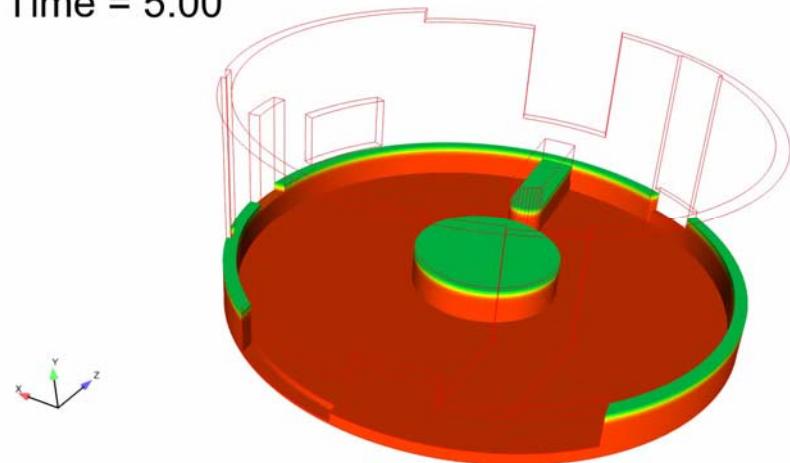
Lower Density Gradients from New Model

- Over many repeats, temperature, pressure, and flow profile are remarkably repeatable
- Imperfectly symmetric fill common
- Pressure rises as foam expands, relaxes at lower corner and stays positive at P2.

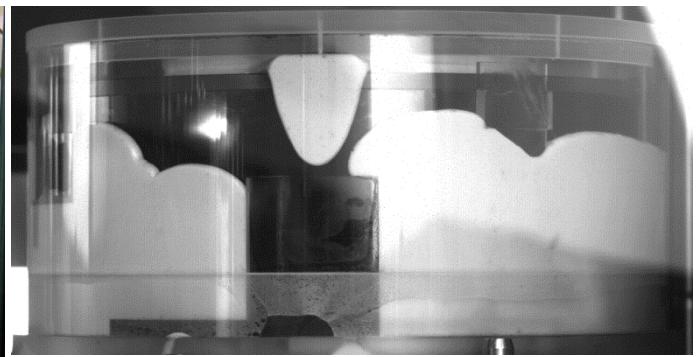
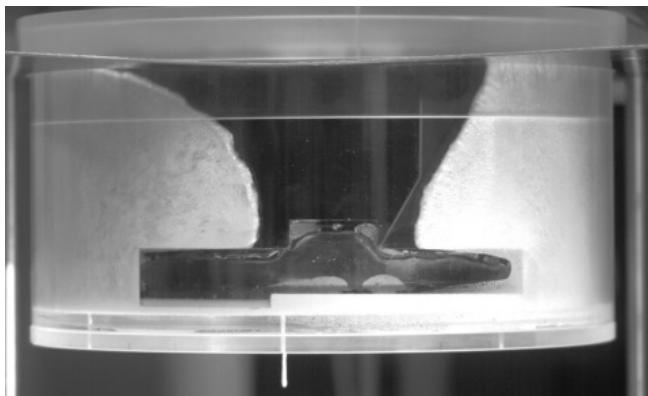
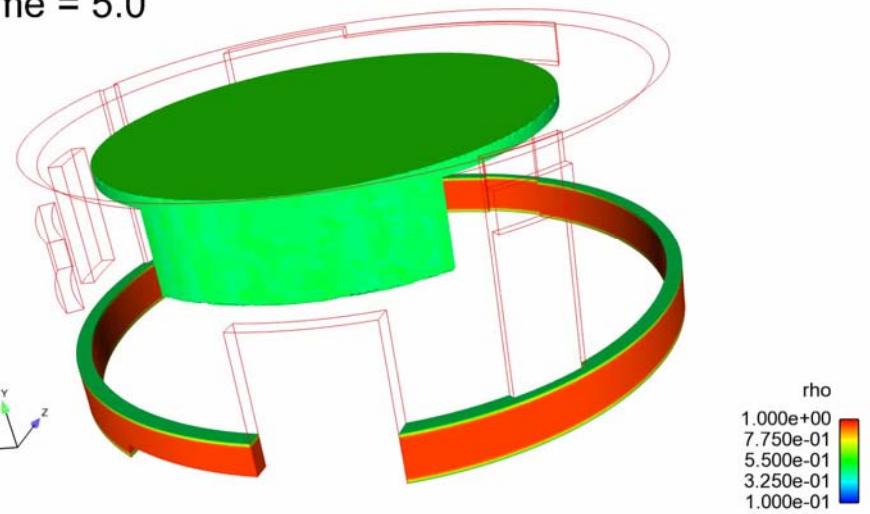


Computational Modeling of Foam Expansion Can Help Design a Mold Filling Process

Time = 5.00

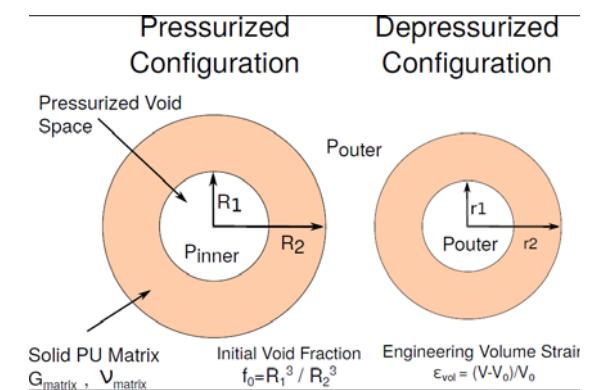
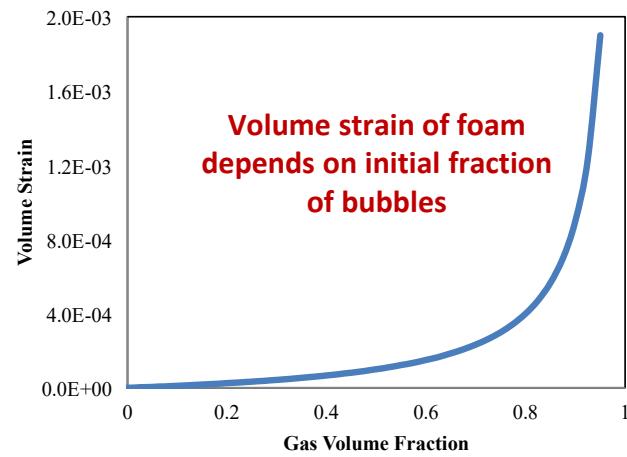
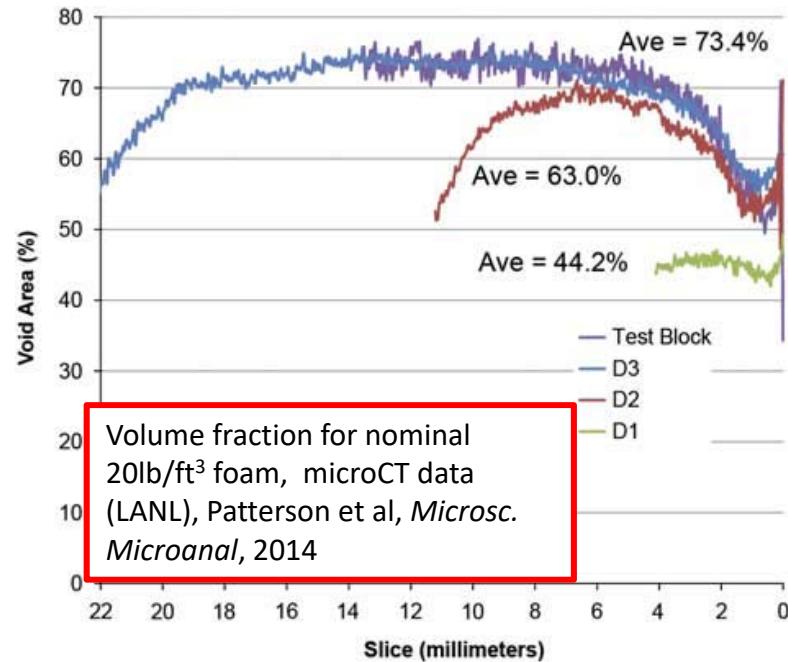
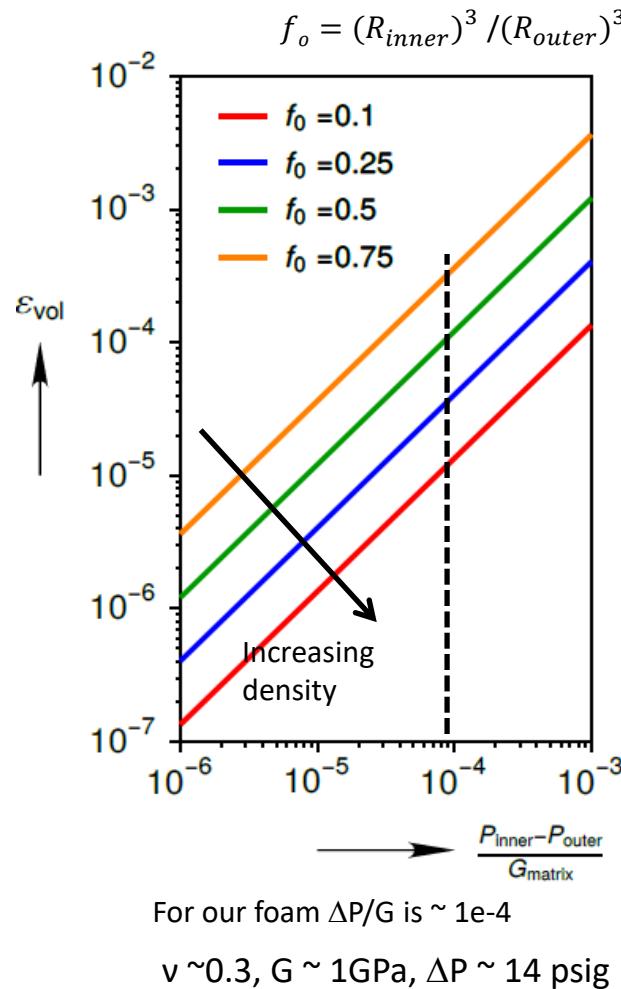


Time = 5.0

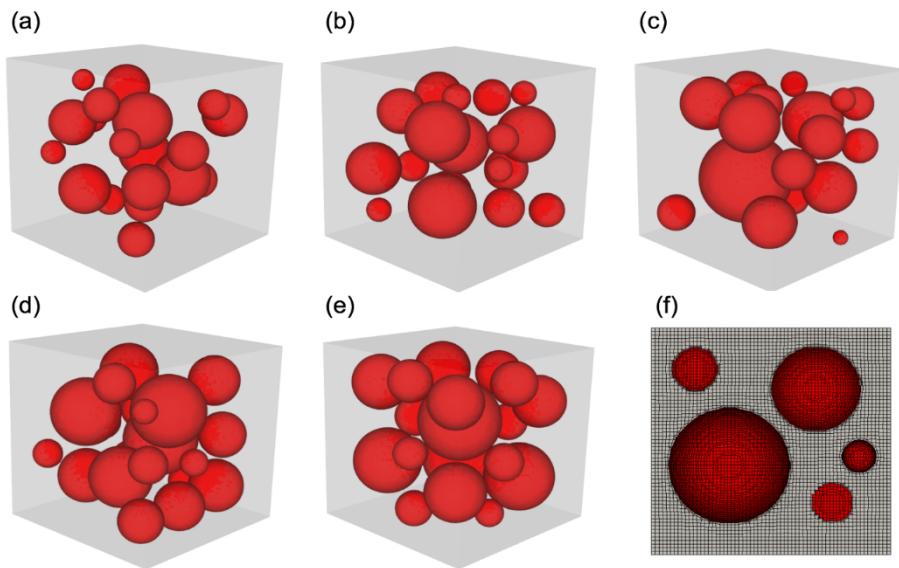


Bubble Depressurization

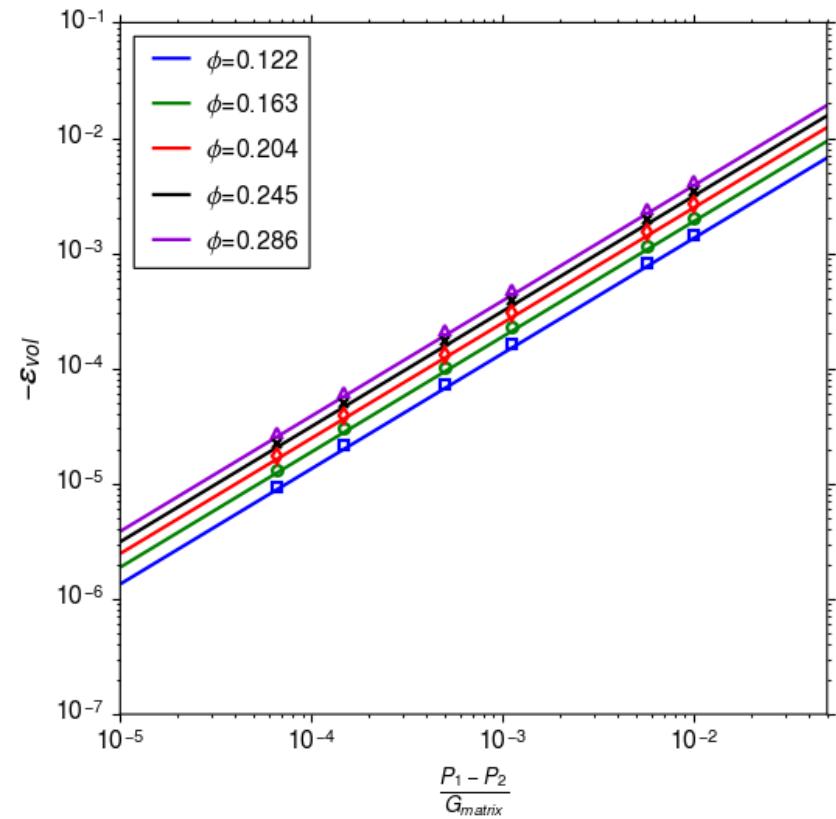
Strain estimates for linear elastic shell as interior pressure decreases from 1.9 atm from 1.0 atm



Micromechanics Validation of the Analytic Model



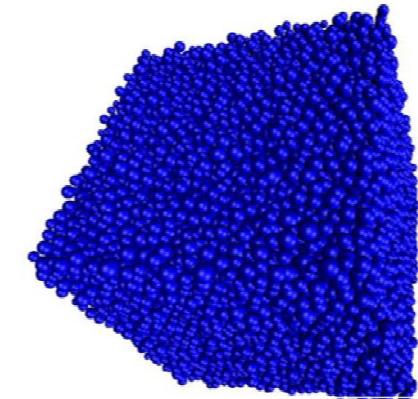
Foam microstructures for (a) 12.2% porosity, (b) 16.3% porosity, (c) 20.4% porosity, (d) 24.5 % porosity, (e) 28.6% porosity, and (f) a cut view of mesh of a 28.6% porosity microstructure.



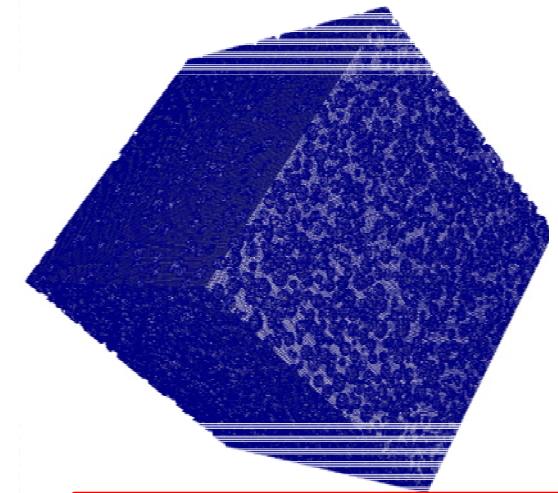
*The Analytic Model Reasonable Well Represents Deformation Due to Depressurization for Isotropic Foams at Low Porosities.
Current Efforts are Extending it to Higher Porosities.*

Conclusions and Future Work

- **Current model is adequate for production calculation**
 - Determining metering, initial placement, voids, gate, and vent location, manufacturing stresses and initial foam shape
 - Current model is “first order.” We are working to make the model more predictive
- **Next generation model needs to include**
 - Equation of state for density approach for gas phase
 - Two-phase CO₂ generation model: solubilized CO₂ in the polymer and CO₂ gas in the bubbles
 - Foam depressurization and its linkage to shape change
- **Include local bubble size and bubble-scale interactions**
 - Predict bubble size with Rayleigh-Plesset equation
 - From the bubble size and number density, predict foam density
 - Bubble-scale modeling to include gelation and gas pressure in density model to make it more predictive for both foaming and aging



0.60 vol fraction Bubbles



Polydisperse bubble microstructure generated with LAMMPS and Sierra/Aria using CDFEM
(Dan Bolintineanu, SNL)