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Polyurethane Foam Expansion, Polymerization and Bubble Pressurization

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SAND2016-????
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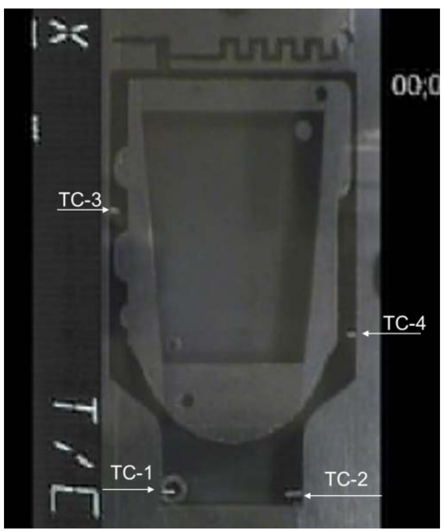
Introduction

Overarching Goal: **Cradle-to-grave model for foaming, vitrification, cure, aging**

Focus on moderate density PMDI foams

Injection, foaming and initial curing at lower T

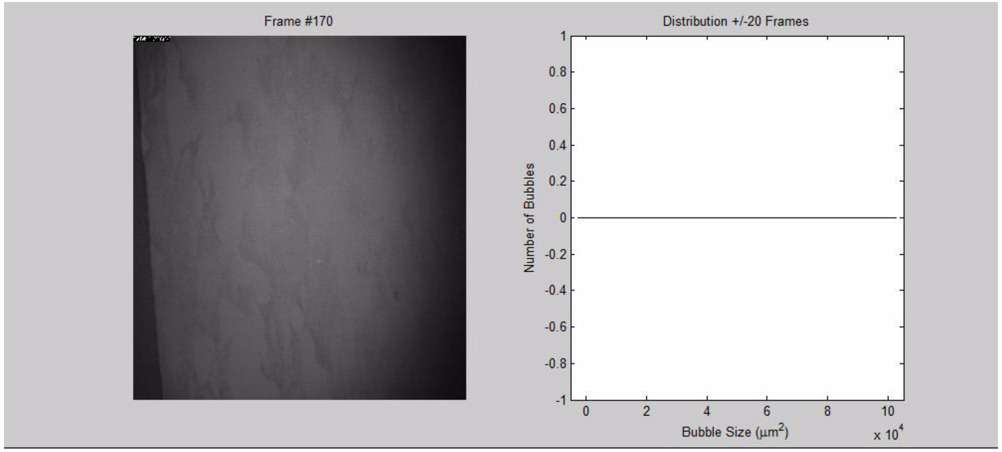
Oven time at higher T to make sure it is fully cured



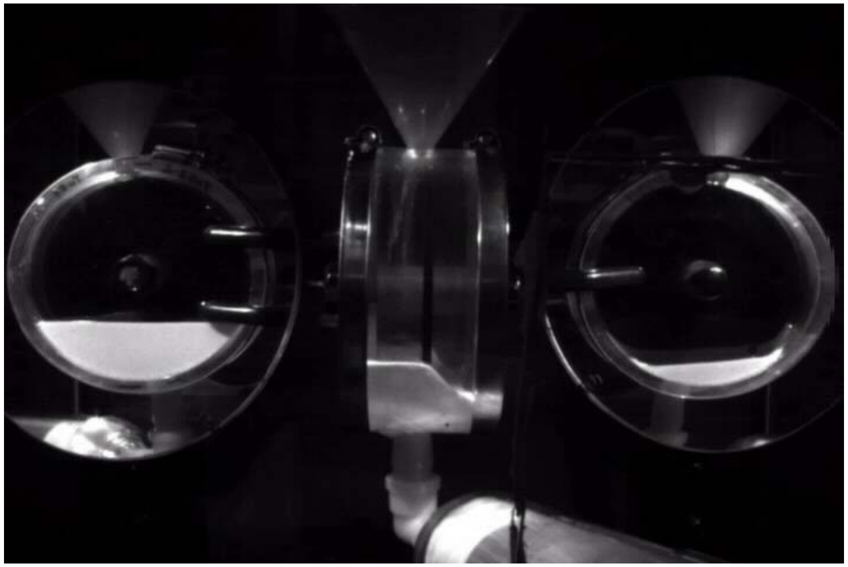
Remove from mold – predict cure and thermal stresses

Predict shape and size over years

Foam Filling is Complex



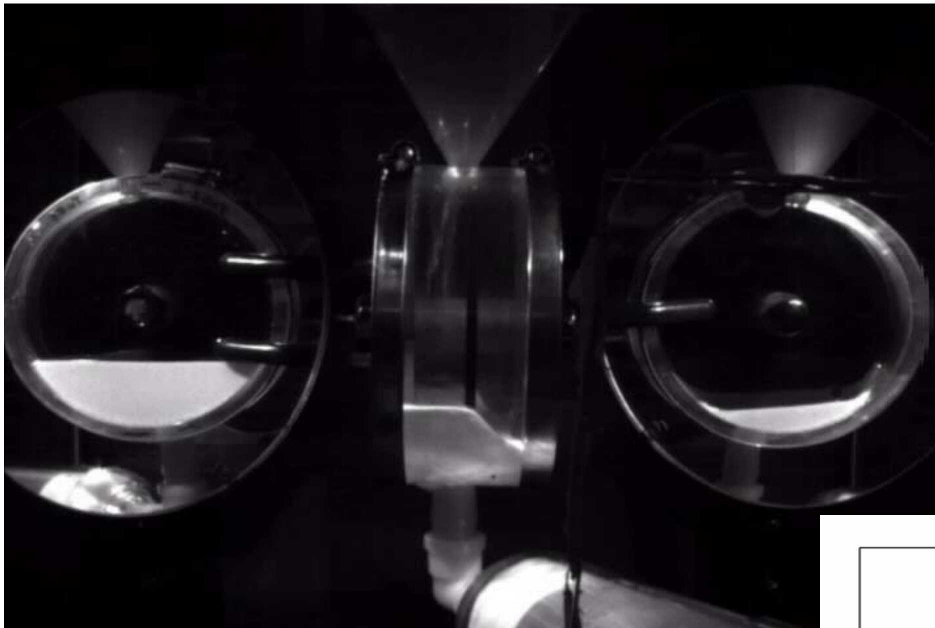
Foam front moving past camera, with bubble sizes at transparent wall determined with image processing.



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

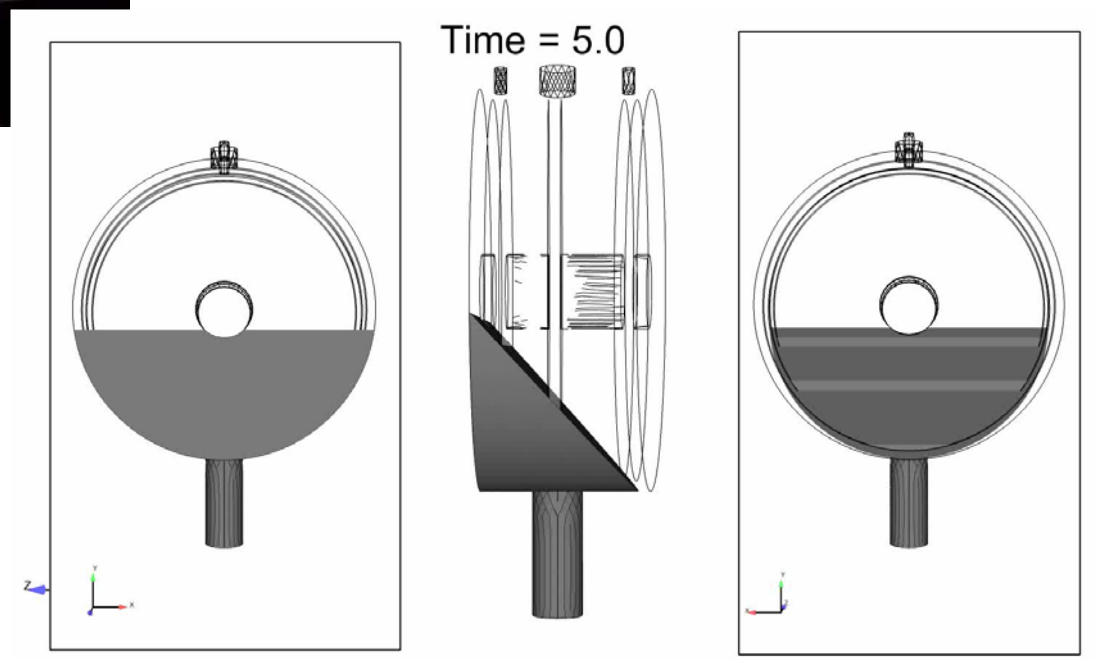
- PMDI is used as an encapsulant for electronic components and lightweight structural parts, to mitigate against shock and vibration.
- **We would like to develop a computational model to help us understand foam expansion for manufacturing applications and how inhomogeneities effect the structural response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

Foam Filling Simulation of Complex Part with Plates



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**

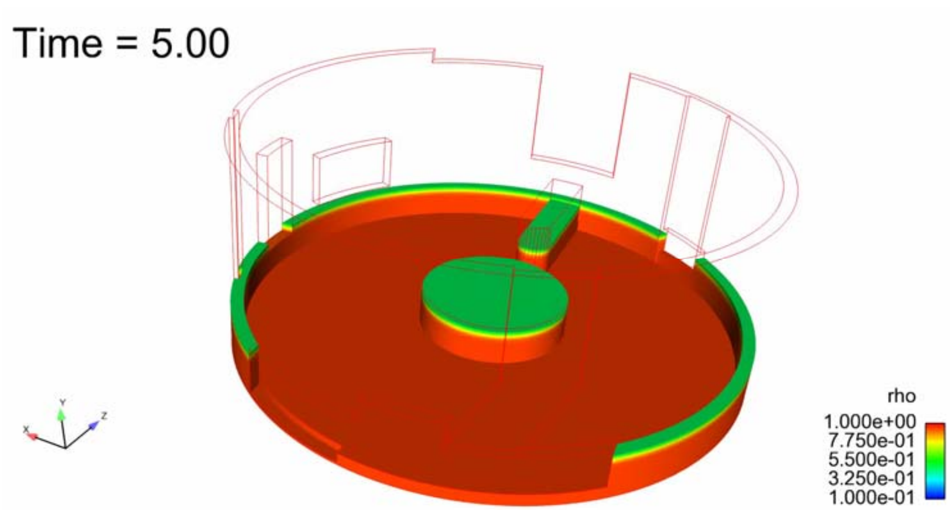


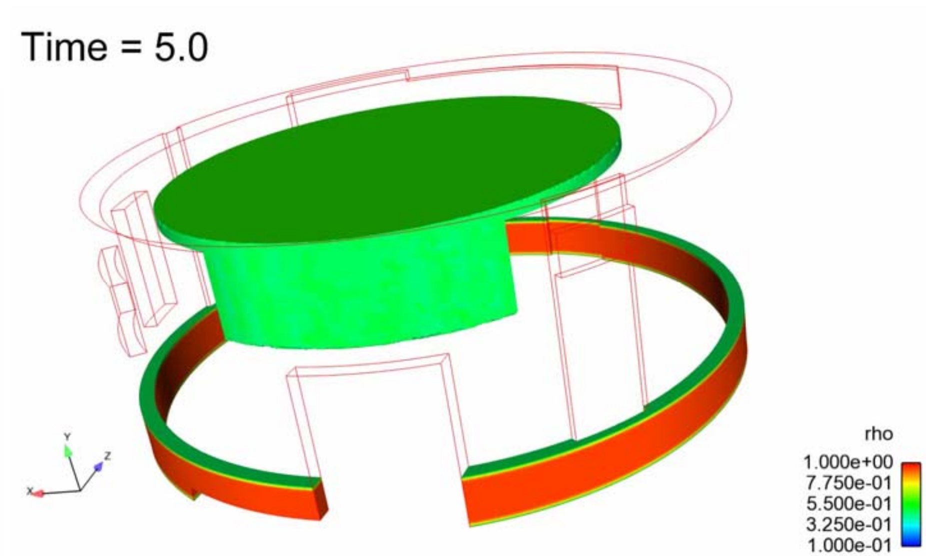
Rao et al., "Polyurethane kinetics for foaming and polymerization" in review, *AICHE Journal*., November 2016

Rao et al., " A Kinetic Approach to Modeling the Manufacture of High Density Polyurethane Structural Foam: Foaming and Polymerization," SAND2015-8282

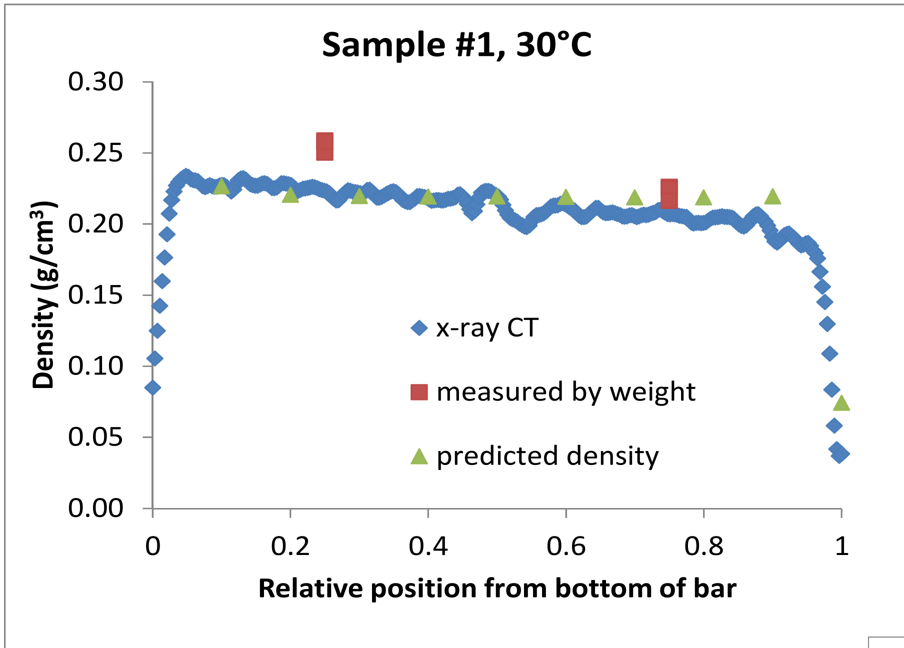
Rao et al, "A Level Set Method to Study Foam Processing ," *IJNMF*, 2012

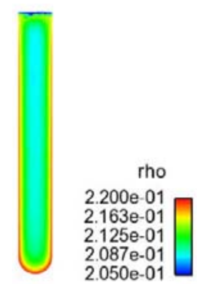
Computational Modeling of Foam Expansion Can Help Design a Mold Filling Process



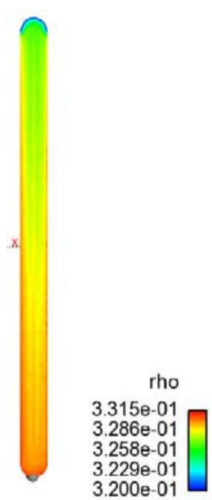


Density Study for Structural Foam PMDI-10

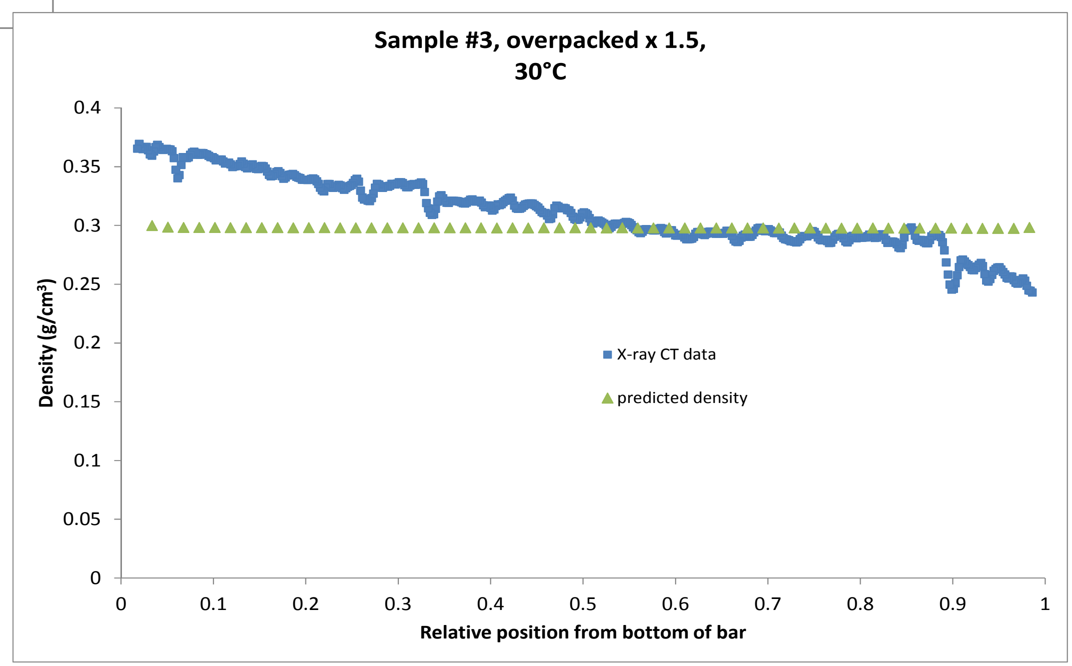




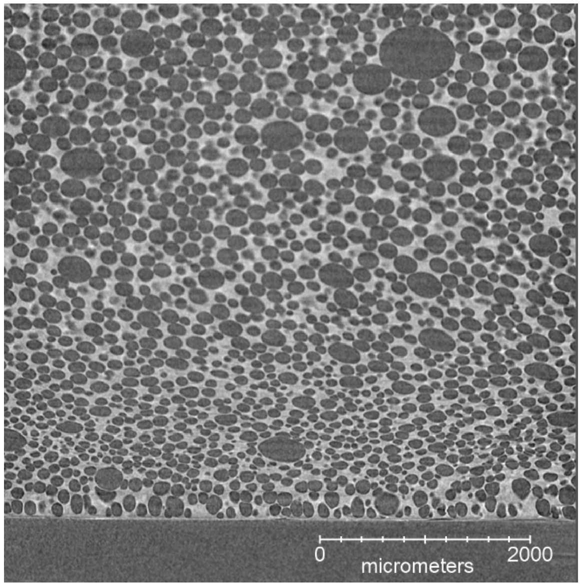
- Free rise foam density gradients. Plots are shown at the centerline of the foam cylinder
- Cylinder is under filled to give the free rise density

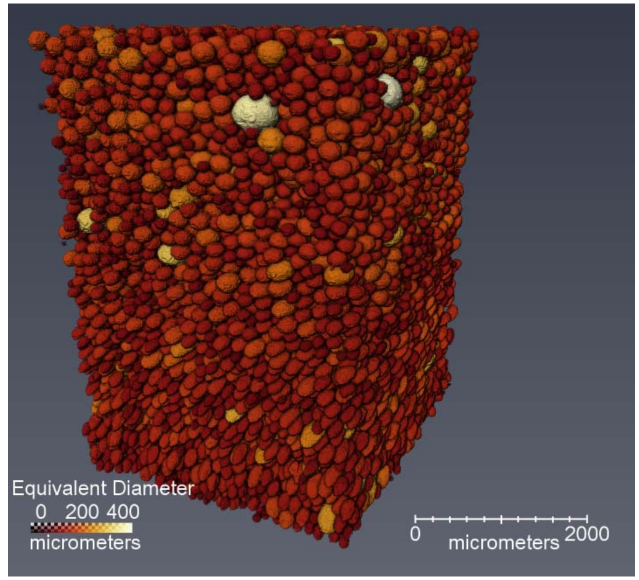


- Over packed (1.5) foam density gradients. Plots are shown at the centerline of the foam cylinder
- Self-closing vent lets air out, but keeps foam in for pressurization



CT Microstructure of Bubbles from Large Complex Mold

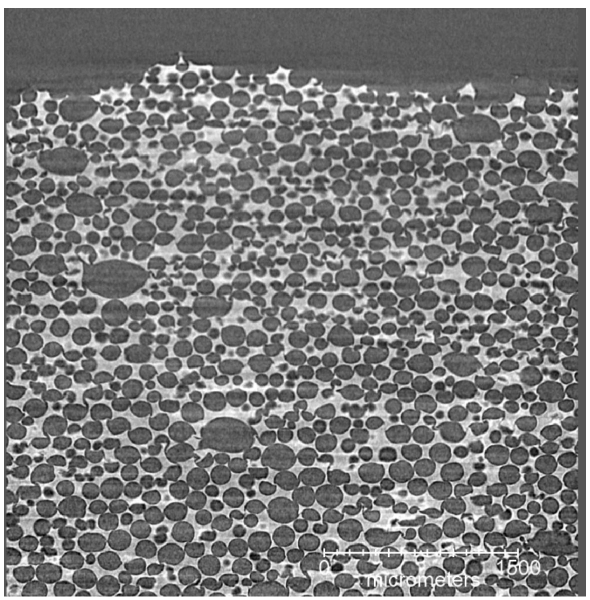


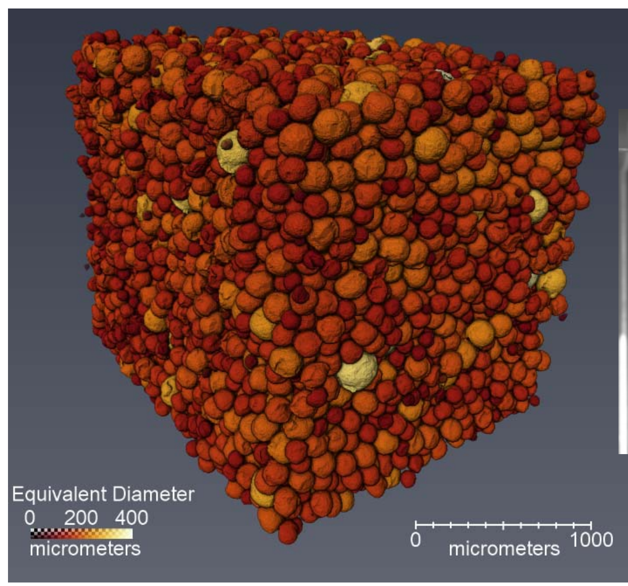


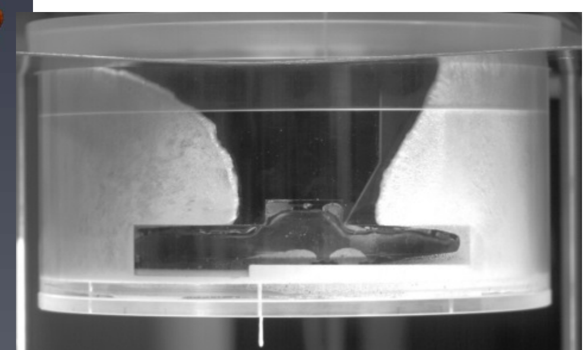
Sample 1 top

Foam microstructure

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



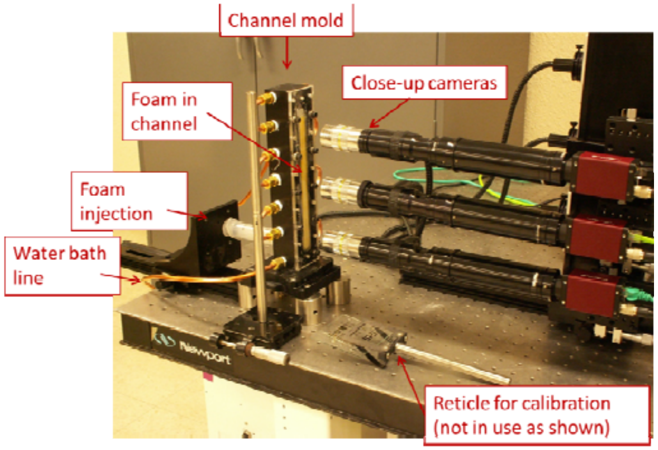




Sample 1 bottom

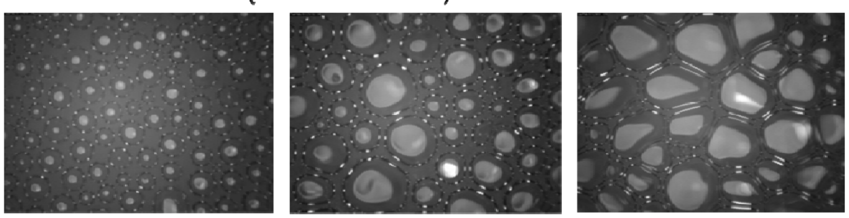
Brian M. Patterson, LANL, July 2016

Study of the Evolution of Bubble Size

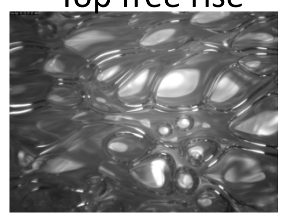


- Three cameras record bubbles at transparent wall (top, middle, and bottom of a column) as foam fills the column
- Light area in pictures below are where the wall is wetted by the bubble – edges are dark lines dashed with bright spots (makes difficult to automatically analyze)
- Image processing developed to analyze – checks by hand shows software good until late times when the bubbles distort severely
- Bubbles nominally about 200-300 microns in diameter
- Size and shape evolve in time, depend on temperature, foam density
- Over packing the foam helps keep the bubbles small and round
- Under packed foam often ends up with highly distorted bubbles near leading front

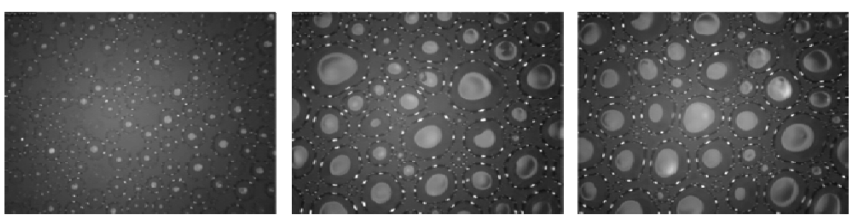
PMDI-4 free rise (bottom camera)



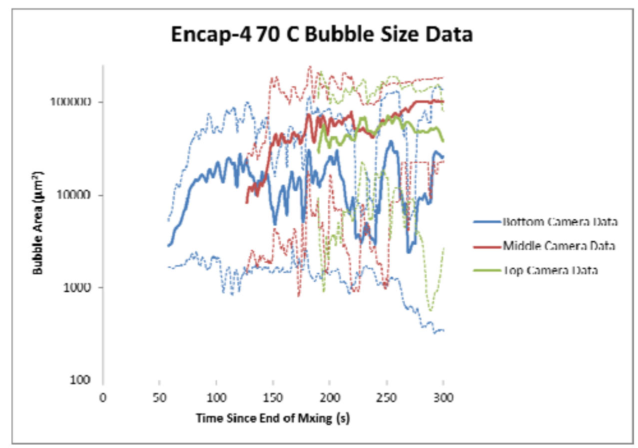
Top free rise



PMDI-4 packed to 8pcf (bottom camera)

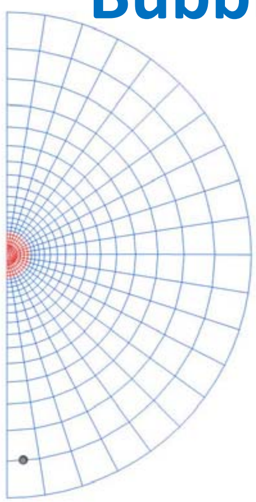


Time=79.5 s Time=152 s Time=266 s since end of mixing

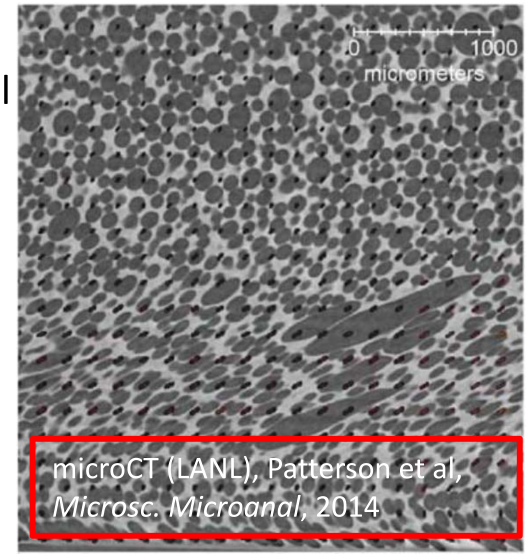


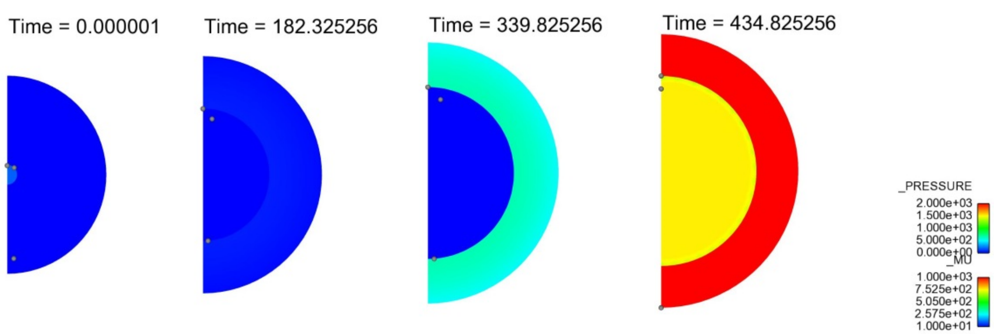
Results of image processing. Solid lines are mean value. Dotted lines indicate top and bottom 10% of values to indicate spread.

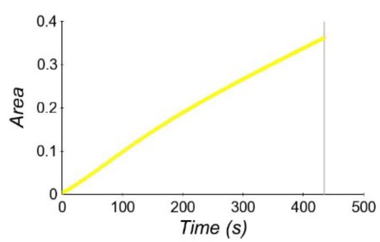
Bubble Expansion in a Polymerizing Fluid

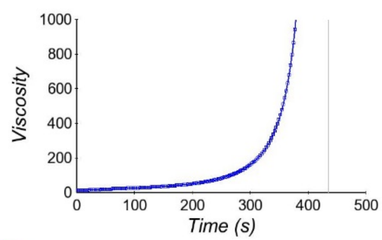


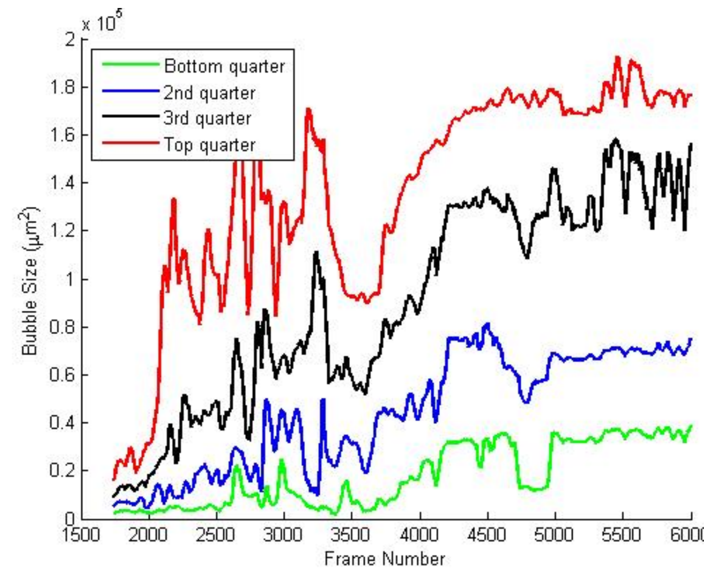
- Bubble grows as CO_2 enters the bubble (VLE model)
- Growth is halted abruptly once the polymer reaches the gel point and the viscosity diverges
- Post-gelation, bubble pressurization is observed
- ALE mesh is robust over shape change
- Data shows the correct trends when compared to experiment











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

ASC PE&M

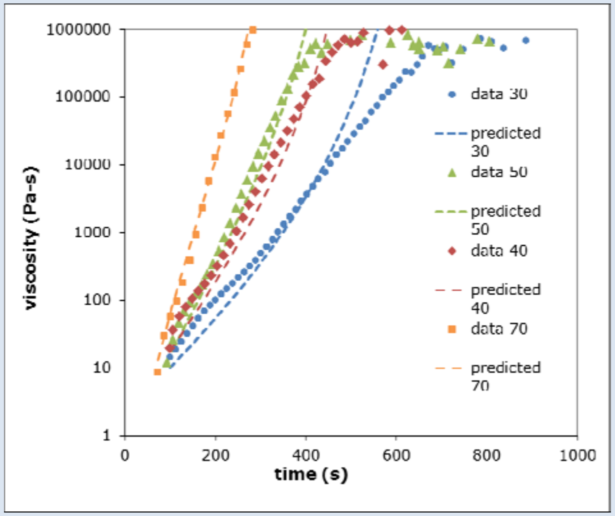
Model Foam Viscosity as f(ξ,φ)

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.

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

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

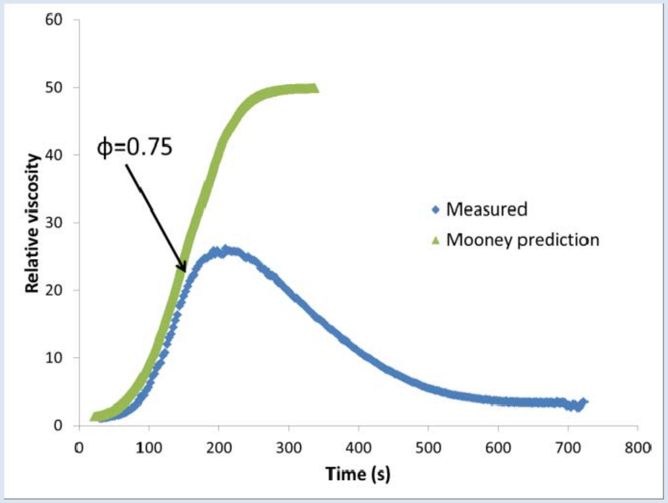


Relate foam viscosity to continuous phase viscosity

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

$$\mu_\varphi = \mu_{polymer} \exp\left(\frac{\varphi_g}{1-\varphi_g} \right)$$

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



Newer Foam Expansion: Two-phase Carbon Dioxide Models

Water balance in the liquid phase (mol H_2O/volume total):

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

Carbon dioxide balance in the liquid phase(mol CO_2/volume total):

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

Bubble conservation equation: it advects

Carbon dioxide balance in the gas phase (mol CO_2/volume total?):

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

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

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

Carbon dioxide balance in the gas phase (mass CO_2/volume bubbles):

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

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):

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

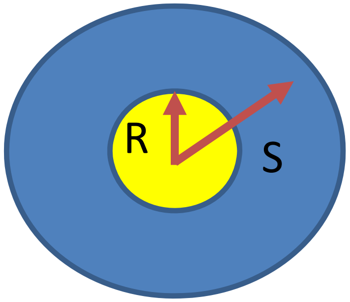
Gas Volume Fraction (volume foam/volume total):

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

Foam Density relationship is the same as before:

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

Influence Volume Approach (IVA)



Interchange between bubbles and liquid phase occurs at interface

$$S_{pg} = 3\frac{\varphi}{R} D_g \frac{\partial C}{\partial R}\Big|_{r=R}$$

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

IVA approach assumes a linear profile of CO_2 in the fluid (blue):

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

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

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

Advection of Number Density Equation:

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

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

Nomenclature

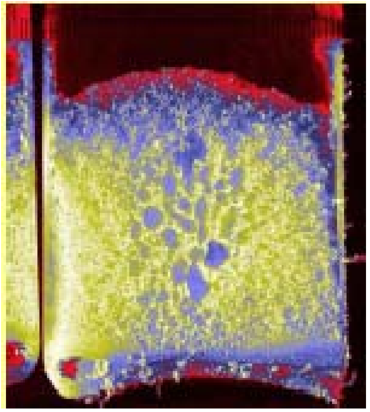
- n = nucleation sites/total volume (the number, *N*, is constant but the density changes over time (#/cc)
- m_{in} = initial mass injected (g)
- K_H = Henry's law coefficient

Equations of Motion Include Evolving Material Models

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

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

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



NMR imaging shows coarse microstructure (Altobelli, 2006)

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

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

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

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

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

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

Including Bubble-Scale Effects

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

Existing equation with minor mods

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

Existing equation with mods including source

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

New equation similar to liquid

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

New equation for bubble gas density

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

New equation for bubble number density

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

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

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

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

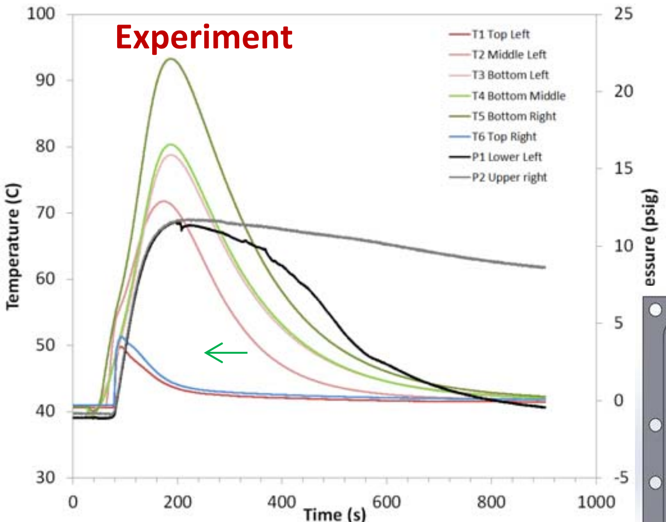
Source terms from bubble scale:

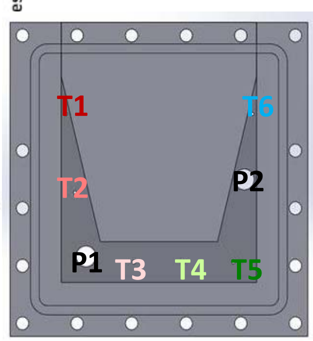
$$S_v = \frac{1}{4\eta_{polymer}}((\rho_{gas} \Re T / M_{CO_2} - p) - \frac{2\sigma}{R_{av}})$$

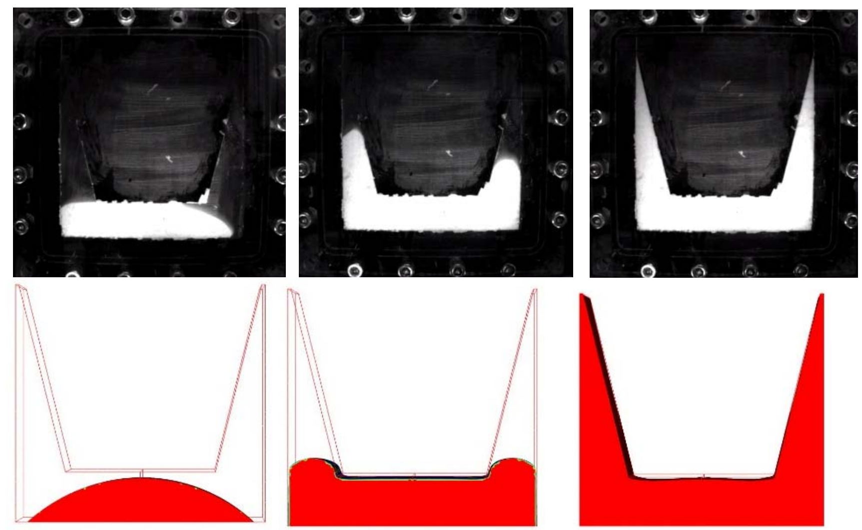
$$S_{pg} = 3 \frac{\varphi}{R_{av}} D_{CO_2} \frac{C_{CO_2} - K_H \rho_{gas} \Re T / M_{CO_2}}{\Delta r}$$

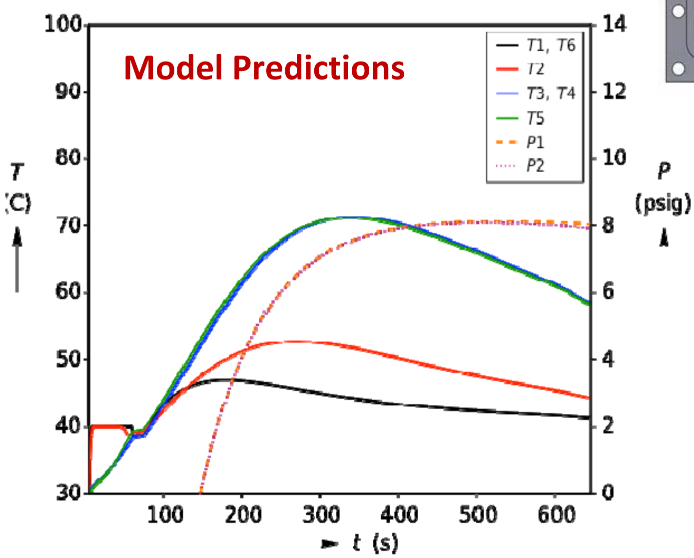
Lower Density Gradients from New Model

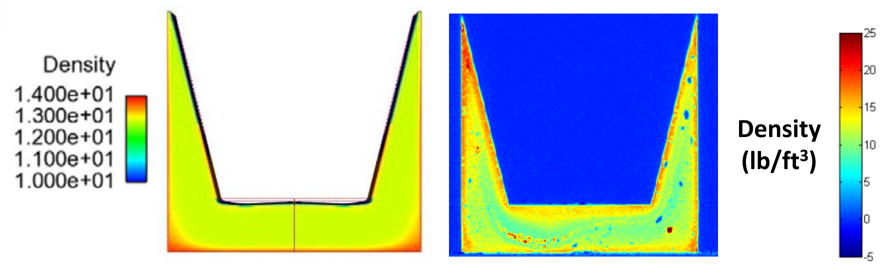
- Over many repeats, temperature, pressure, and flow profile are remarkably repeatable
- Imperfectly symmetric fill common
- Pressure rises as foam expands, relaxes at lower corner and stays positive at P2.









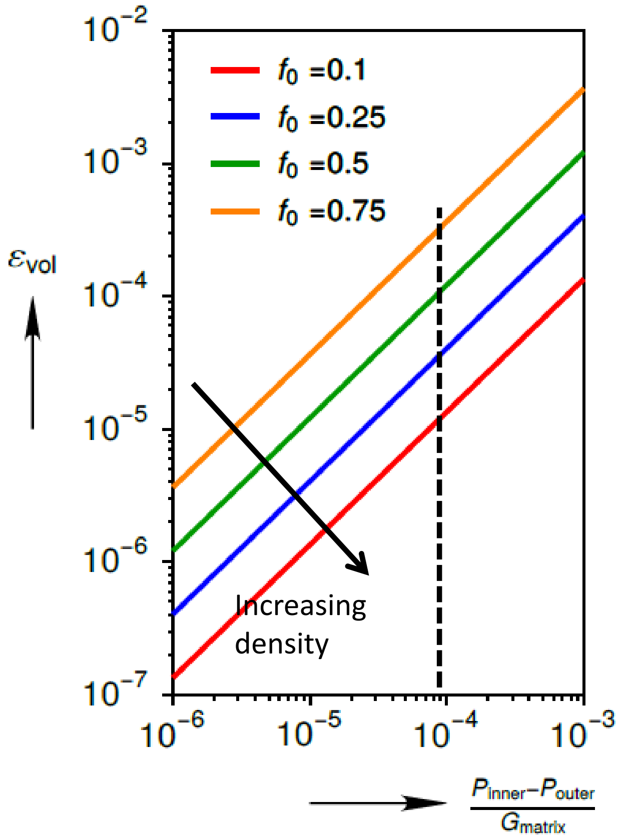


Model **X-ray CT Data (Thompson, 2016)**

Bubble Depressurization

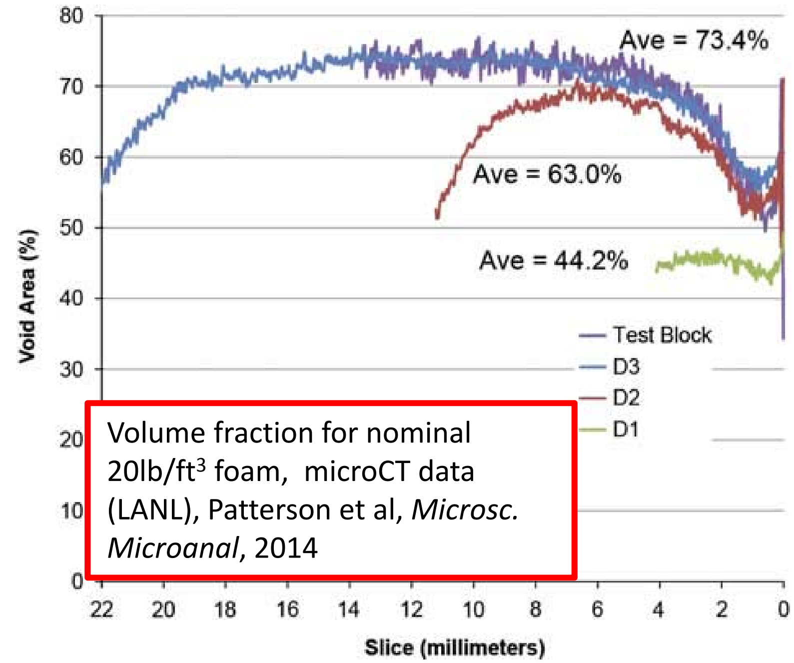
Strain estimates for linear elastic shell as interior pressure decreases from 1.9 atm from 1.0 atm

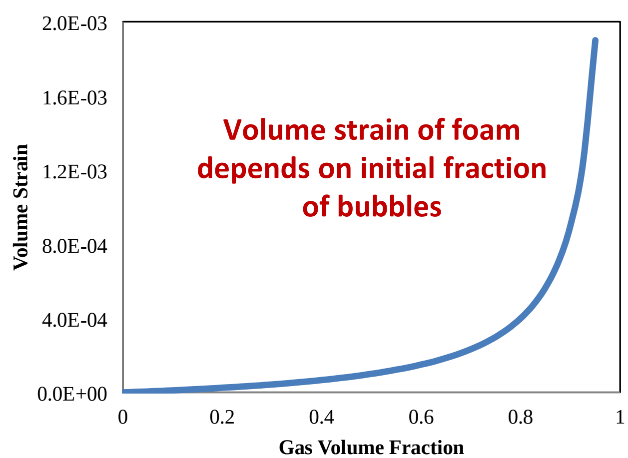
$$f_o = (R_{inner})^3 / (R_{outer})^3$$

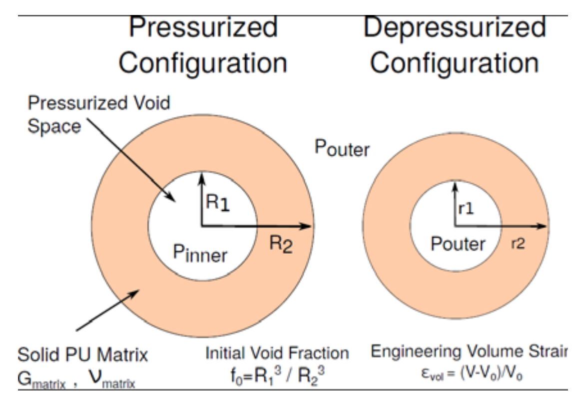


For our foam ΔP/G is ~ 1e-4

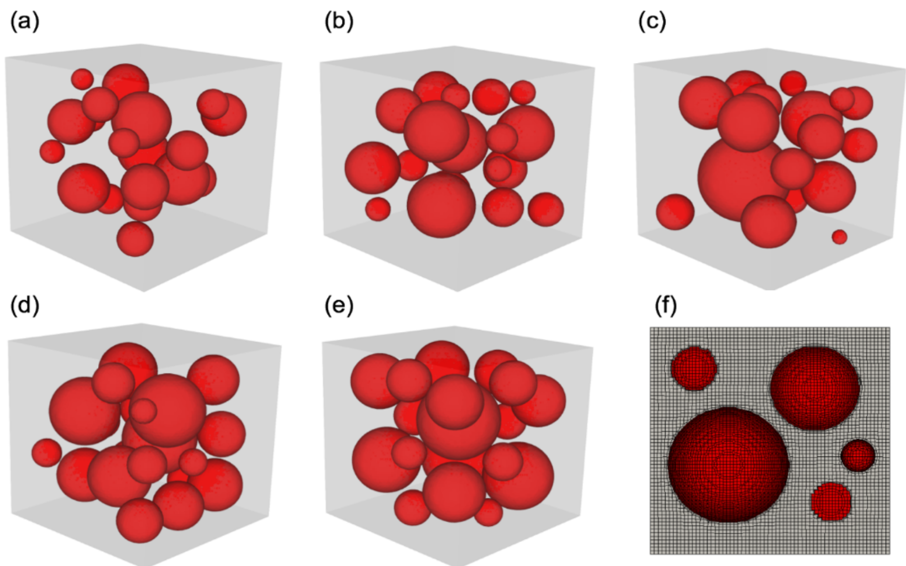
ν ~0.3, G ~ 1GPa, ΔP ~ 14 psig



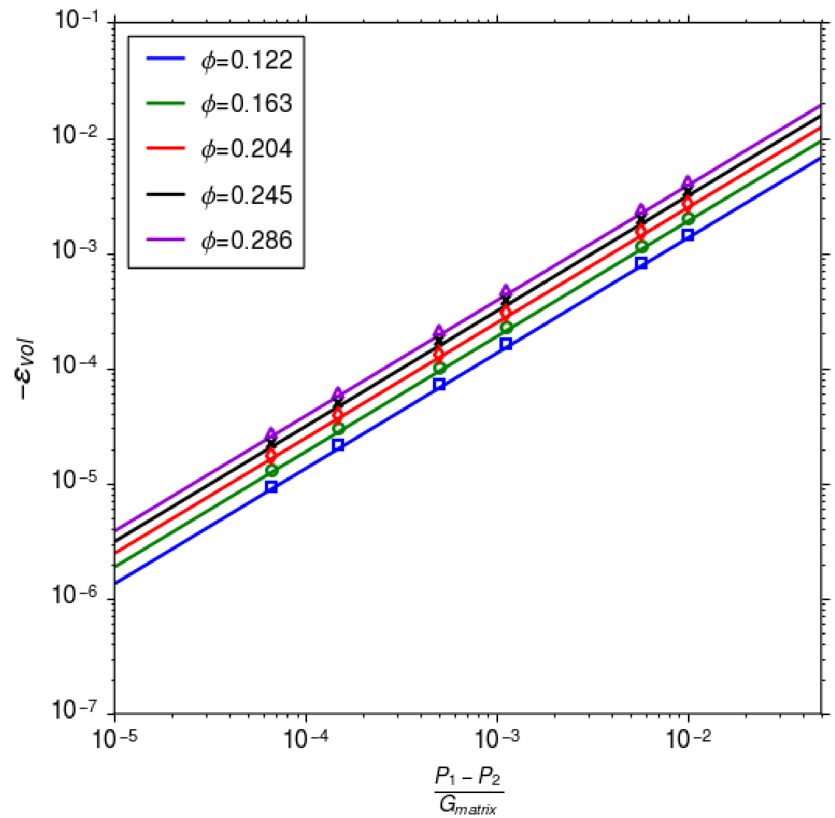




Micromechanics Validation of the Analytic Model

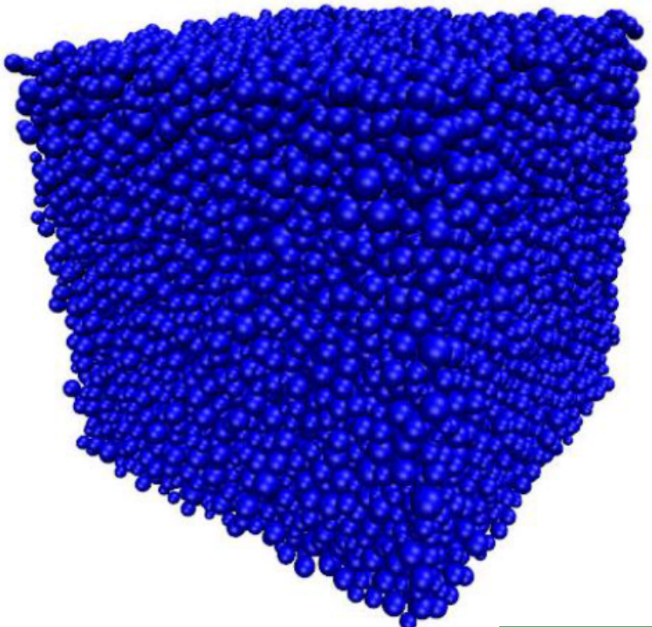


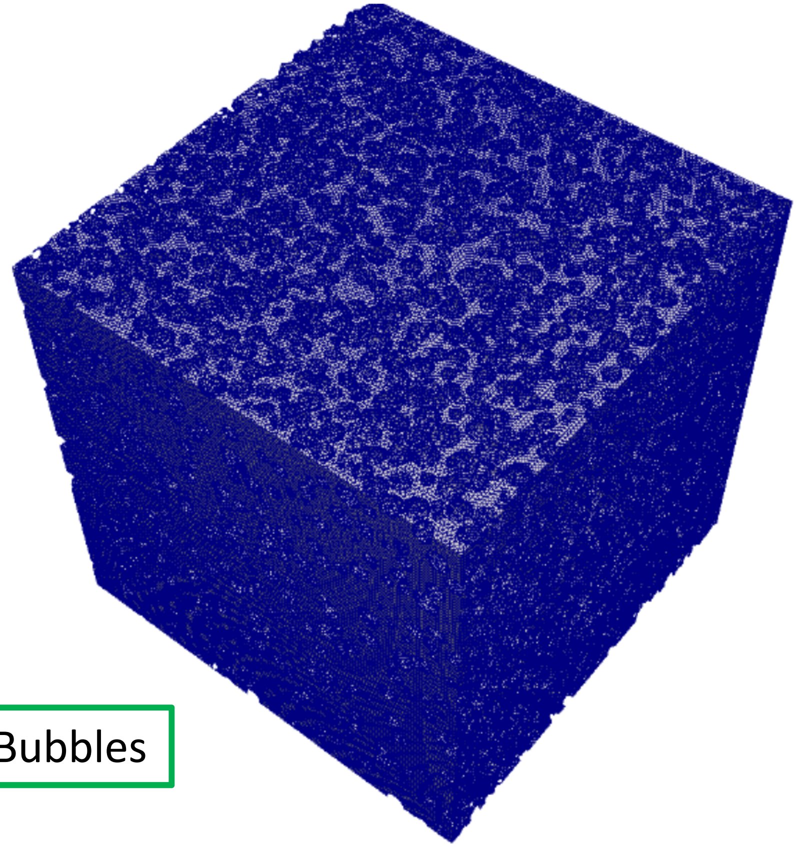
Foam microstructures for (a) 12.2% porosity, (b) 16.3% porosity, (c) 20.4% porosity, (d) 24.5 % porosity, (e) 28.6% porosity, and (f) a cut view of mesh of a 28.6% porosity microstructure.



The Analytic Model Reasonable Well Represents Deformation Due to Depressurization for Isotropic Foams at least at Low Porosities

LAMMPS/Sierra Aria with CDFEM





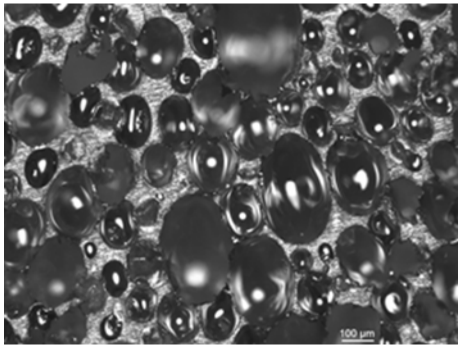
0.60 vol fraction Bubbles

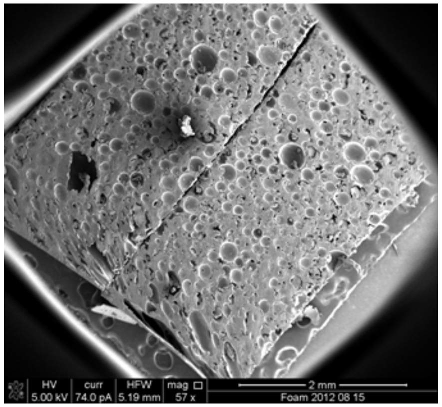
Polydisperse bubble microstructure generated with LAMMPS and Sierra/Aria using CDFEM
(Dan Bolintineanu, SNL)

- Mesh of bubbles and polymers
- Will allow for diffusion calculations including discontinuous concentration jump at the interface
- Will be interesting to try foam drainage and bubble blowing simulations as well

Conclusions and Future Work

SEM of foam showing polydispersity





Bubble at walls are elongated and show coarsening

- **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 CO_2 generation model: solubilized CO_2 in the polymer and CO_2 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