

INCLUDING BUBBLE-SCALE INFORMATION IN CONTINUUM FOAM EXPANSION AND AGING MODELS

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Sandia National Laboratories

Albuquerque, NM

Workshop on Mathematics for Mesoscopic Modeling of Materials (CM4)

Sandia National Laboratories

Albuquerque, NM

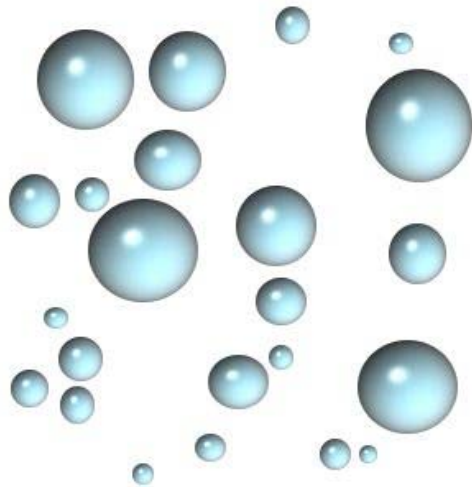
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SAND2016-????C

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What is a Foam?

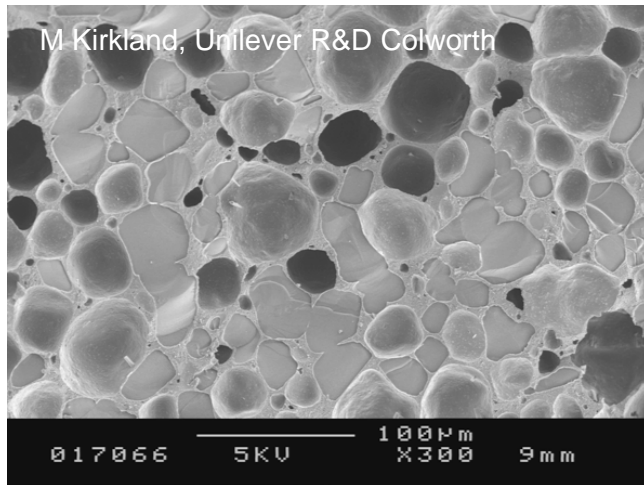


Bubbles

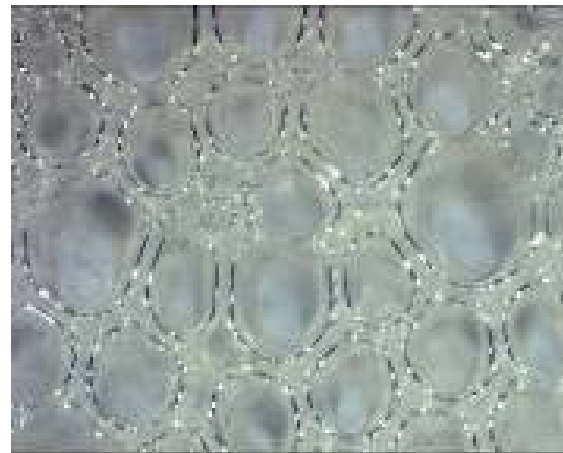


Whipped cream

- A multiphase material of gas bubbles in a liquid or solid matrix
- How do you make a foam?
 - Generate bubbles in a liquid
 - Stabilize them with particles, fat globules, or surfactant
 - Solidify liquid -freezing, polymerization, or phase change – if desired



Ice cream is a foam – that's why it is so much work to make

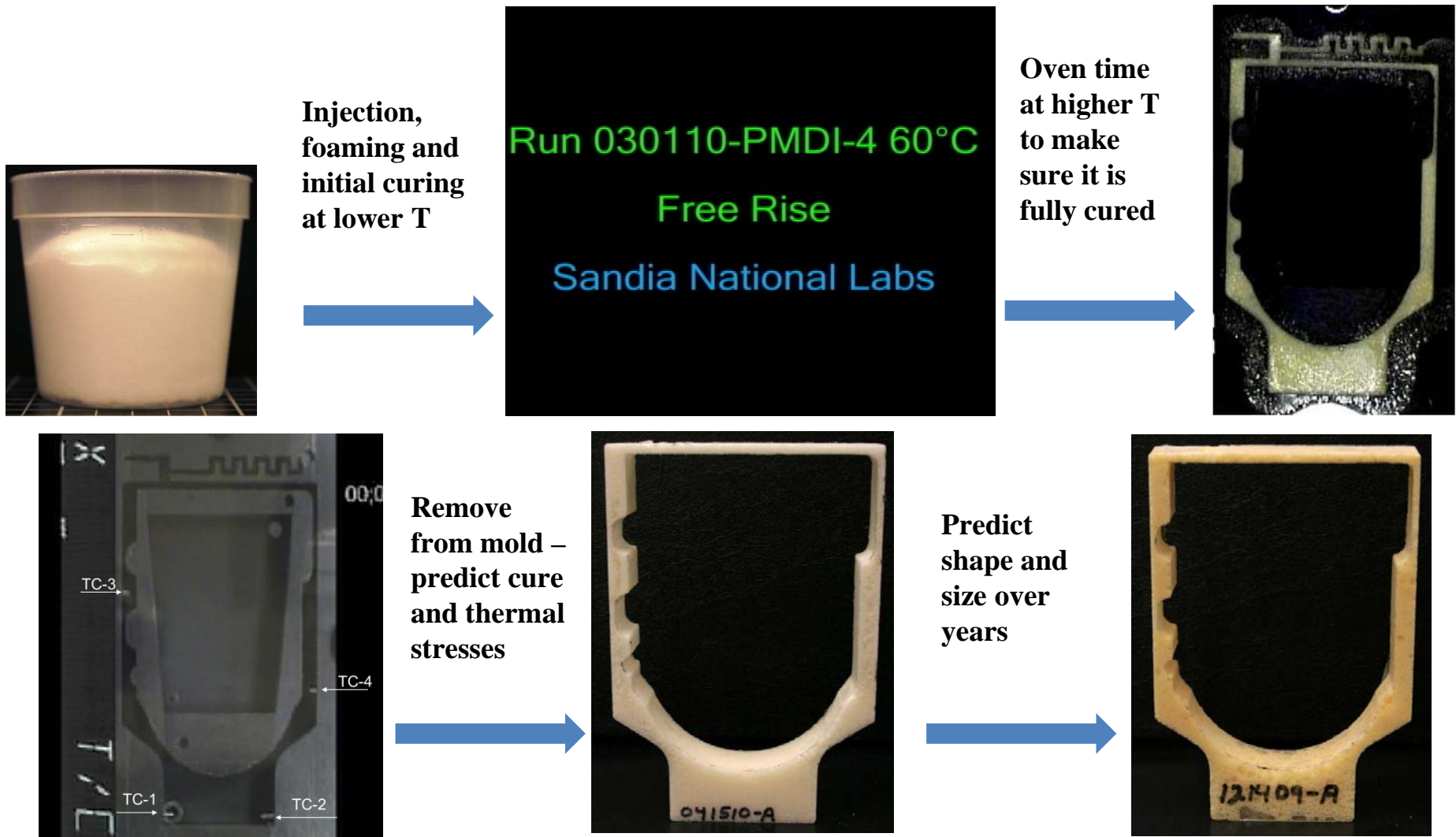


Epoxy foam is a collection of bubbles in polymer

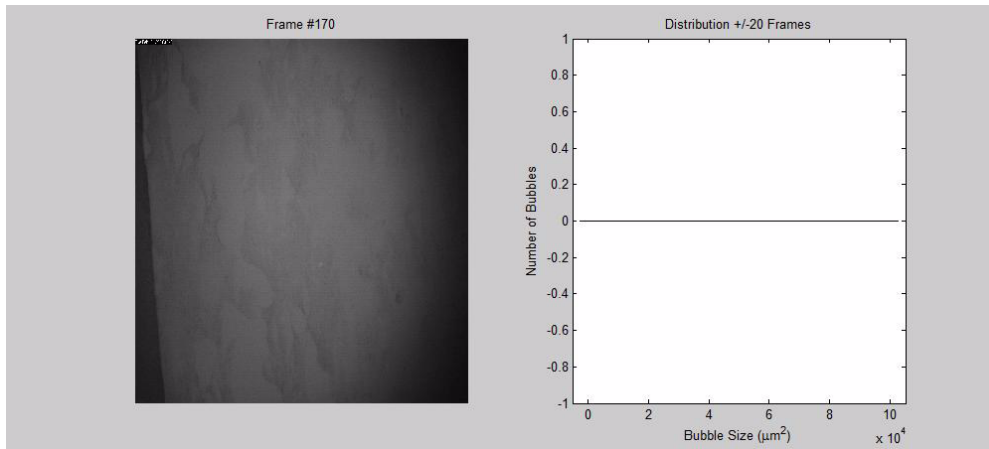
Foams need enough bubbles to jam, e.g. bubbles are touching or it is just a bubbly liquid

Introduction

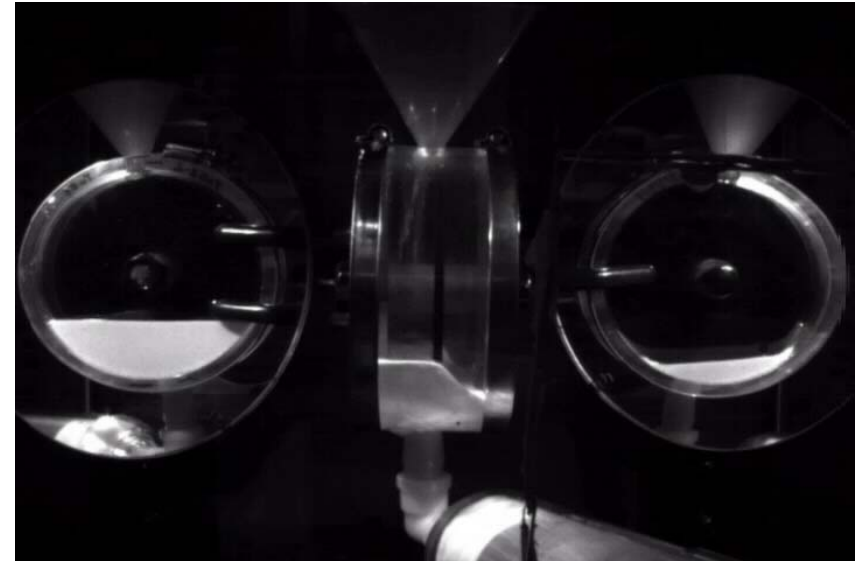
Overarching Goal: Cradle-to-grave model for foaming, vitrification, cure, aging
Focus on moderate density PMDI foams



Foam Filling is Complex



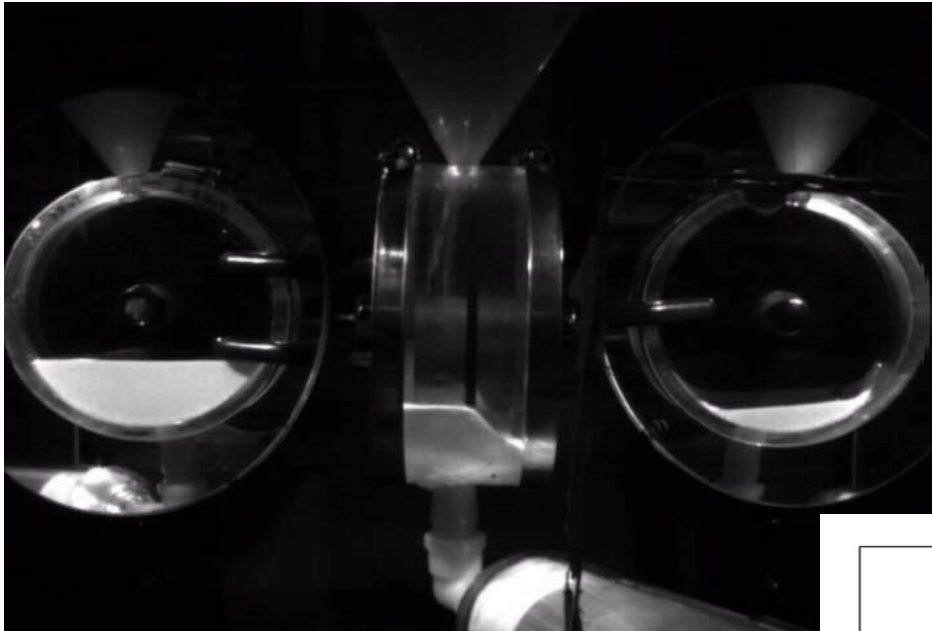
Foam front moving past camera, with bubble sizes at transparent wall determined with image processing.



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



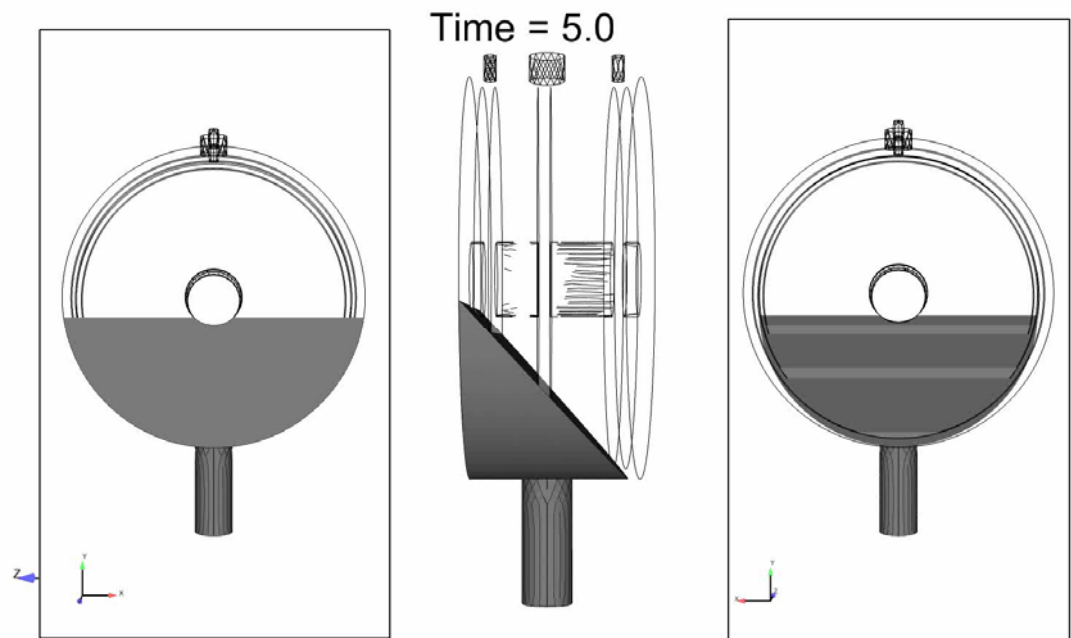
Coupled Finite Element Method/Level Set to Solve Foam Dynamics

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

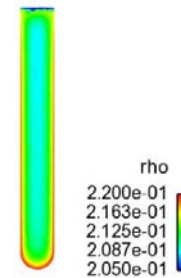
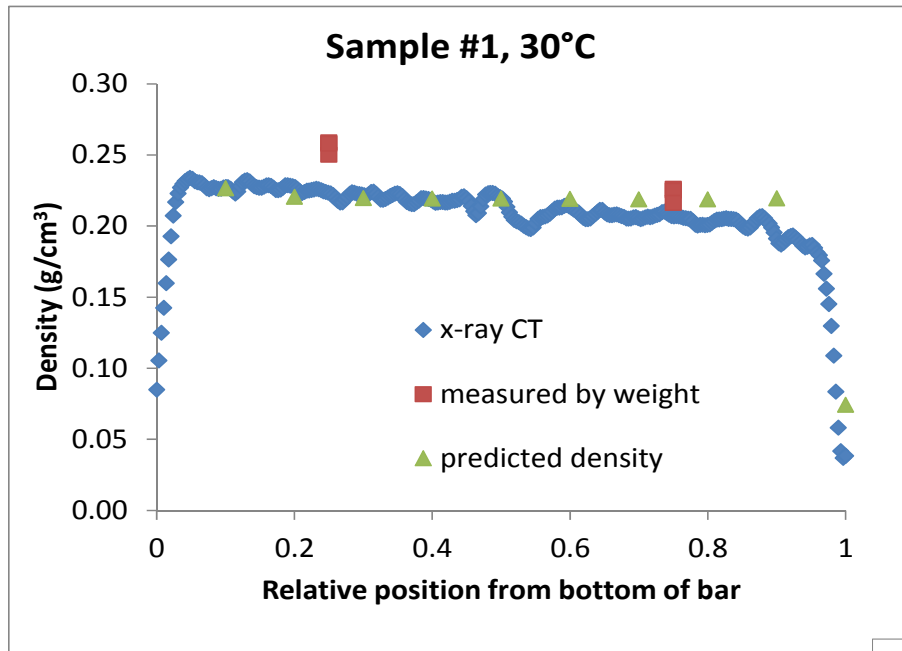
Rao et al., "Polyurethane kinetics for foaming and polymerization" submitted, *AIChE Journal*., June 2016

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

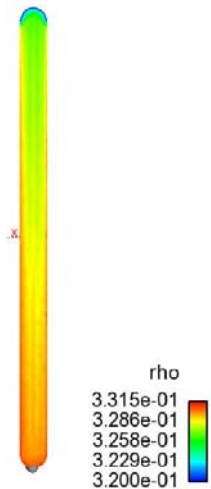
Rao et al, "A Level Set Method to Study Foam Processing," *IJNMF*, 2012



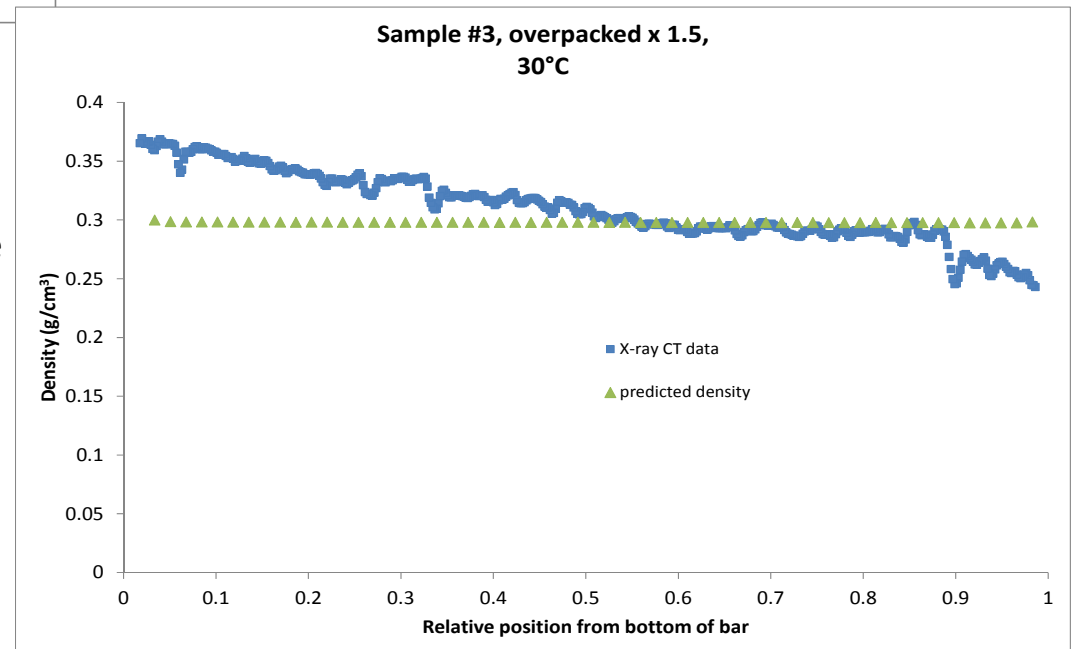
Density Study for Structural Foam PMDI-10



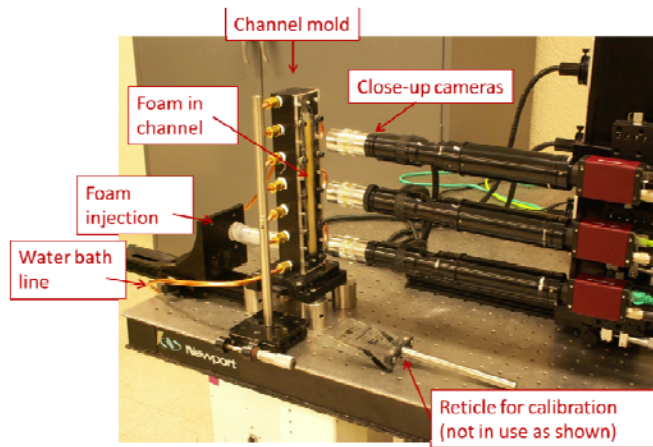
- Free rise foam density gradients. Plots are shown at the centerline of the foam cylinder
- Cylinder is under filled to give the free rise density



- 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

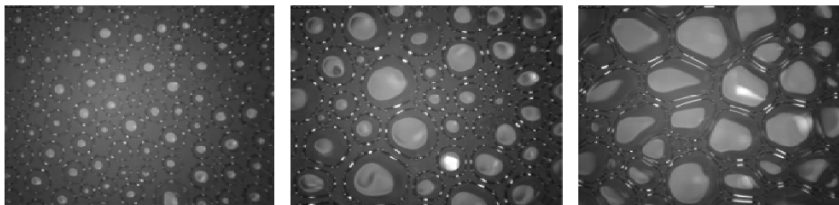


Study of the Evolution of Bubble Size

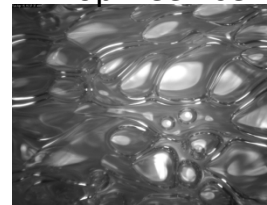


- Three cameras record bubbles at transparent wall (top, middle, and bottom of a column) as foam fills the column
- Light area in pictures below are where the wall is wetted by the bubble – edges are dark lines dashed with bright spots (makes difficult to automatically analyze)
- Image processing developed 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



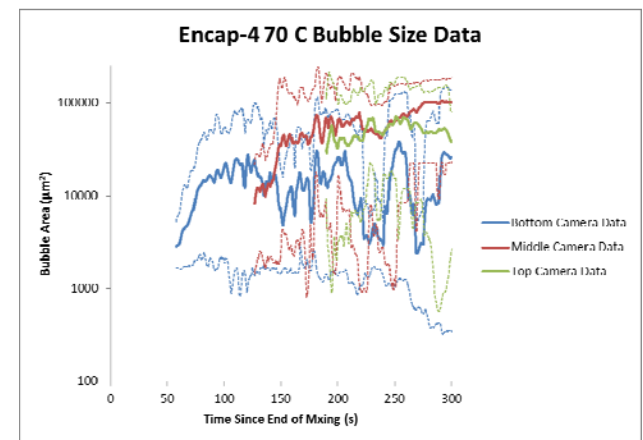
PMDI-4 packed to 8pcf (bottom camera)



Time=79.5 s

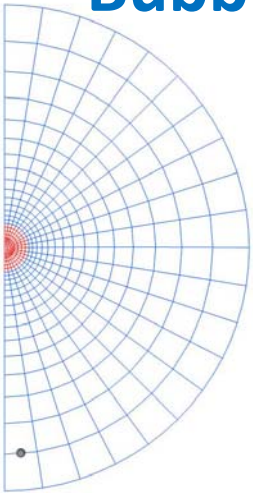
Time=152 s

Time=266 s since end of mixing

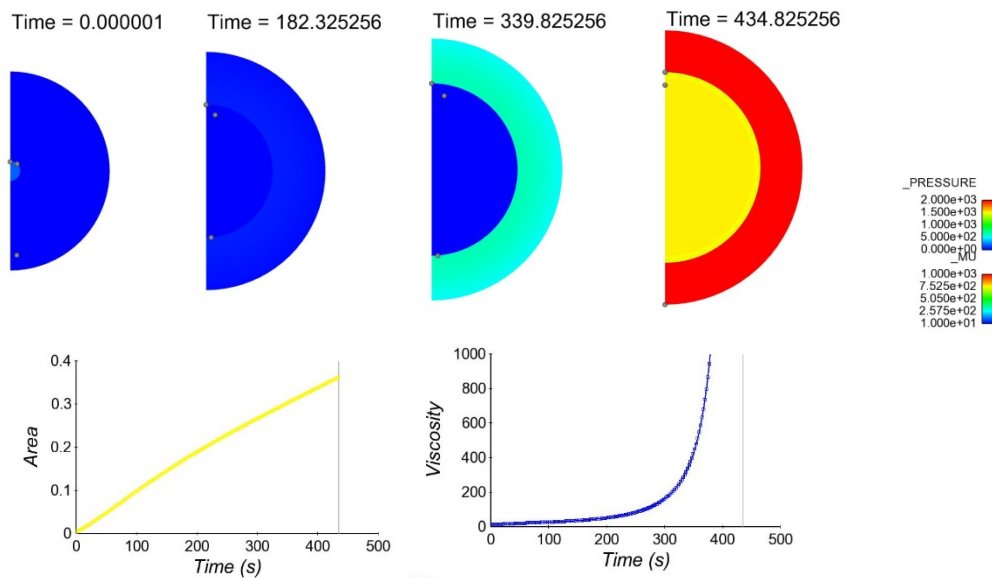
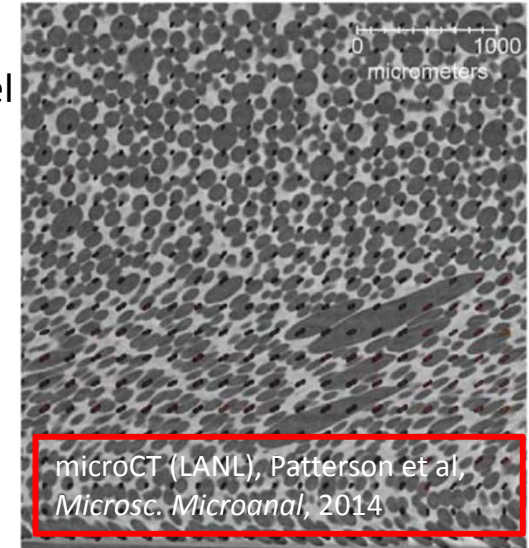


Results of image processing. Solid lines are mean value. Dotted lines indicate top and bottom 10% of values to indicate spread.

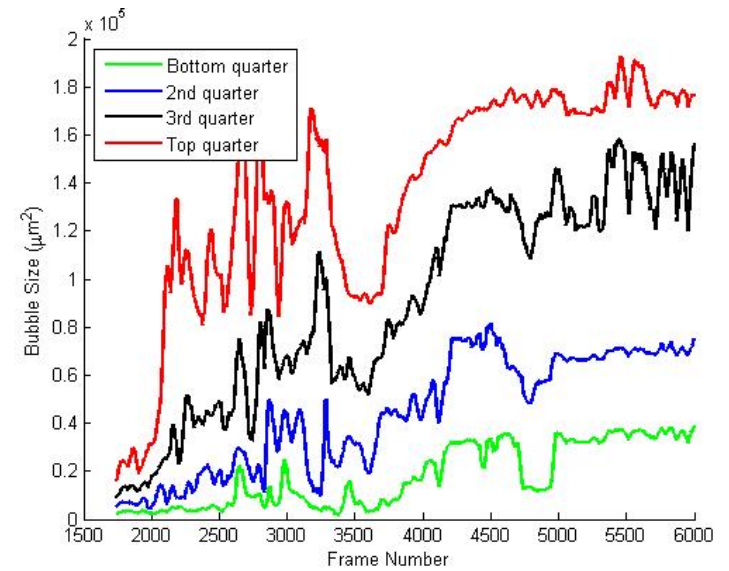
Bubble Expansion in a Polymerizing Fluid



- Bubble grows as CO₂ 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



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



Newer Foam Expansion: Two-phase Carbon Dioxide Models

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

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

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

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

Bubble conservation equation: it advects

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

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

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

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

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:

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

Influence Volume Approach (IVA)

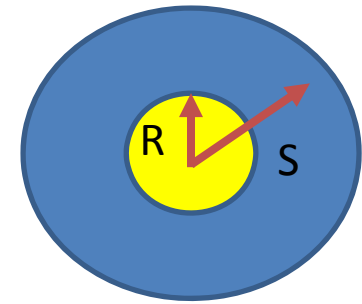
Interchange between bubbles and liquid phase occurs at interface

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

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

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

$$S_{pg} = 3 \frac{\varphi}{R_{av}} D_g \frac{C_{CO_2} - K_H \rho_{gas} \mathfrak{R}T / M_{CO_2}}{\Delta r} \quad \Delta r = \frac{(S_{av}^4 - R_{av}^4) - R_{av}(S_{av}^3 - R_{av}^3)}{S_{av}^3 - R_{av}^3}$$



Advection of Number Density Equation:

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

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

- We can solve an approximate solution based on the initial number and foam density

$$n = \frac{N \rho_{foam}}{m_{in}}$$

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

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

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

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

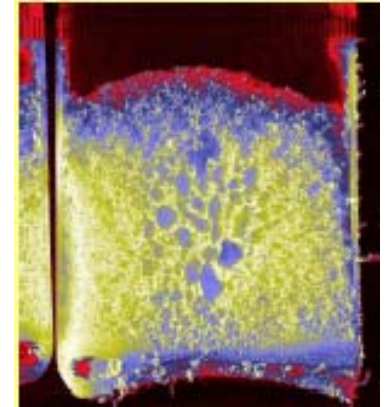
$$\rho C_{pf} \frac{\partial T}{\partial t} + \rho C_{pf} \mathbf{v} \cdot \nabla T = \nabla \cdot (k \nabla T) + \rho \phi_e \Delta H_{rxn} \frac{\partial \xi}{\partial t}$$

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

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

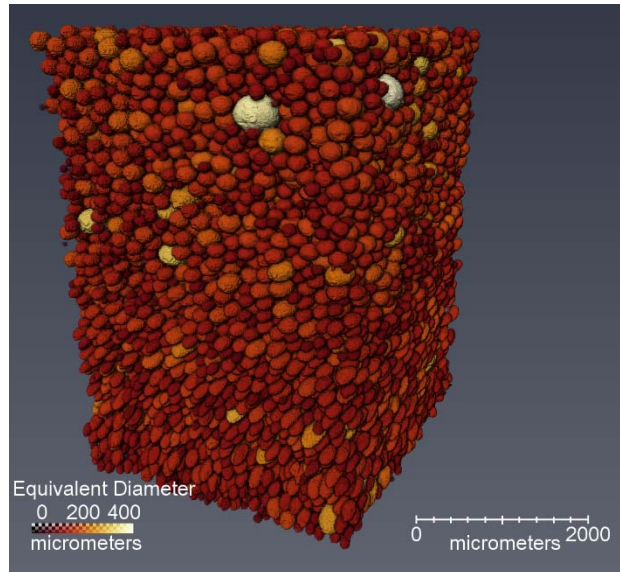
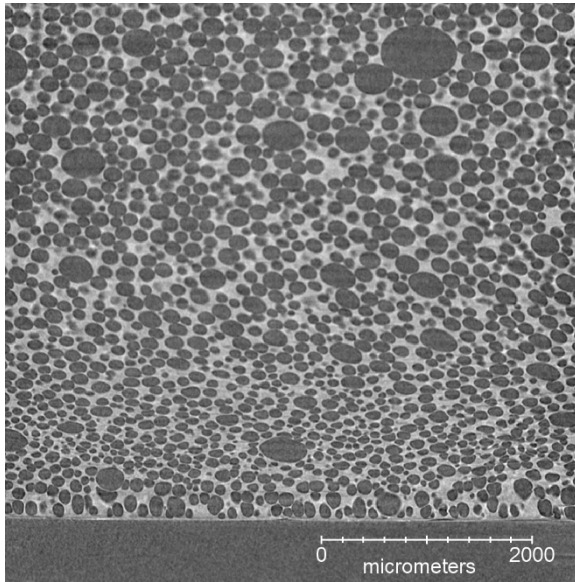
New molar concentration equations for water and carbon dioxide on the next page: kinetics stay the same

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

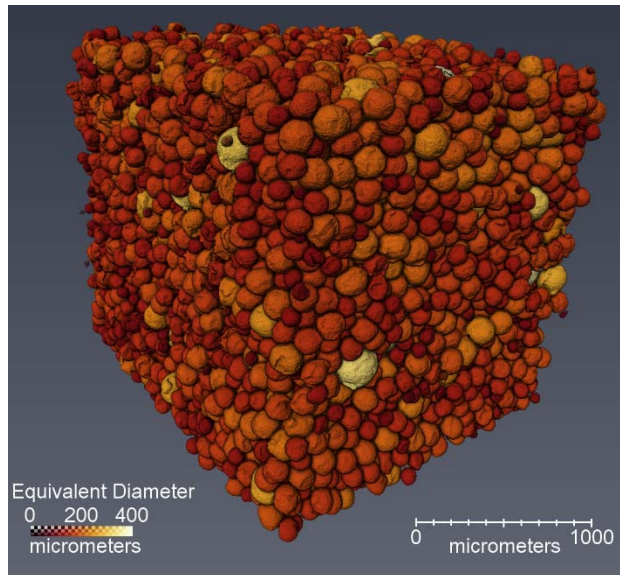
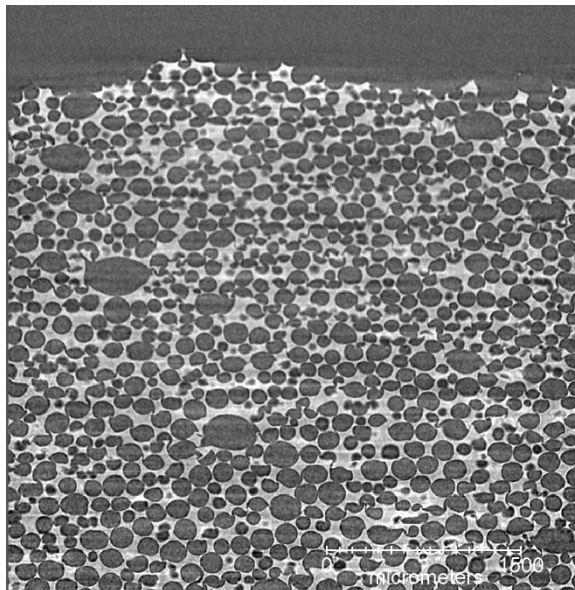


NMR imaging shows coarse microstructure (Altobelli, 2006)

CT Microstructure of Bubbles from Large Complex Mold



Sample 1 top

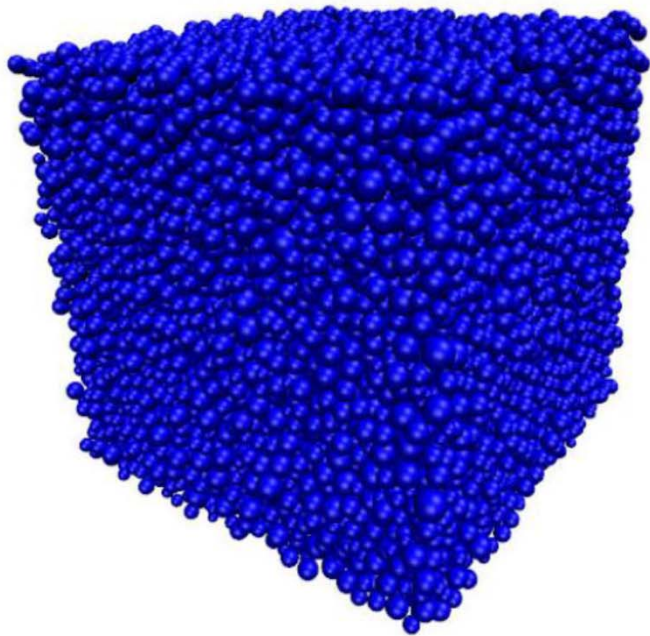


Sample 1 bottom

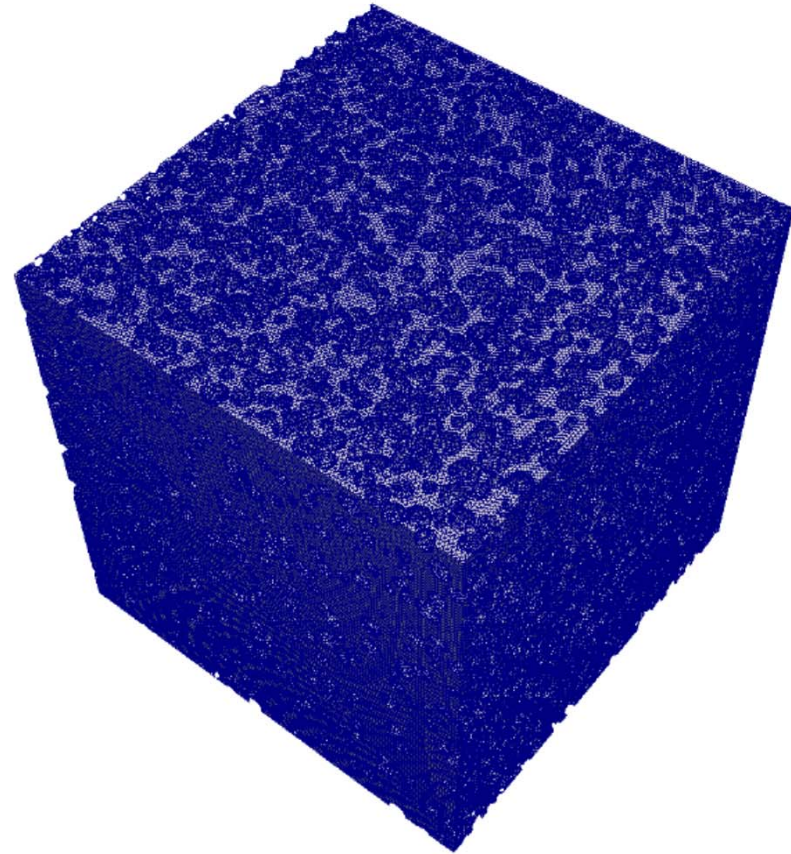
Foam microstructure

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

LAMMPS/Sierra Aria with CDFEM



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



0.60 vol fraction Bubbles

Including Bubble-Scale Effects

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

Existing equation with minor mods

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

Existing equation with mods including source

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

New equation similar to liquid

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

New equation for bubble gas density

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

New equation for bubble number density

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

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

Source terms from bubble scale:

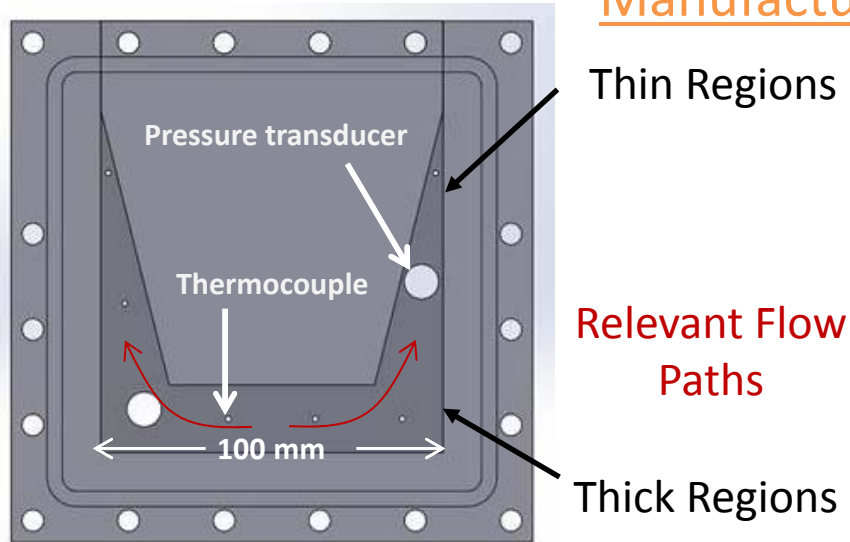
$$S_v = \frac{1}{4\eta_{polymer}} \left((\rho_{gas} \mathcal{R}T / M_{CO_2} - p) - \frac{2\sigma}{R_{av}} \right)$$

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

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

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

Goal: Quantify warpage in a relevant geometry:
Model validation data and physical insight and Measure the Manufacturing Conditions

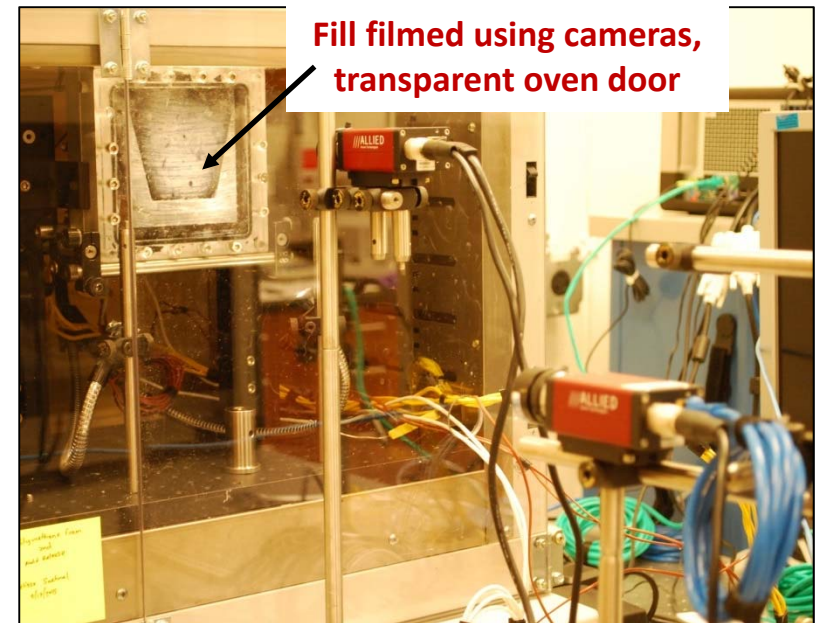


Foaming/Manufacturing Conditions

- **PMDI** (**10 lb/ft³** Free Rise) foam injected at **40 °C**, overpacked to **12.5 lb/ft³**
- After 15 mins, cured in oven at **121 °C** for **4 hrs**

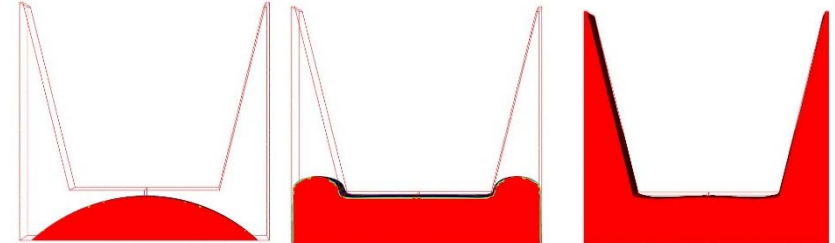
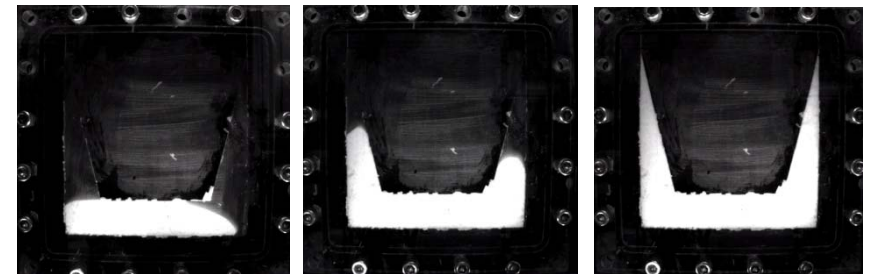
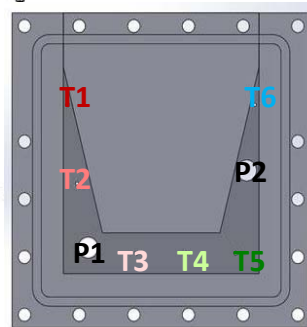
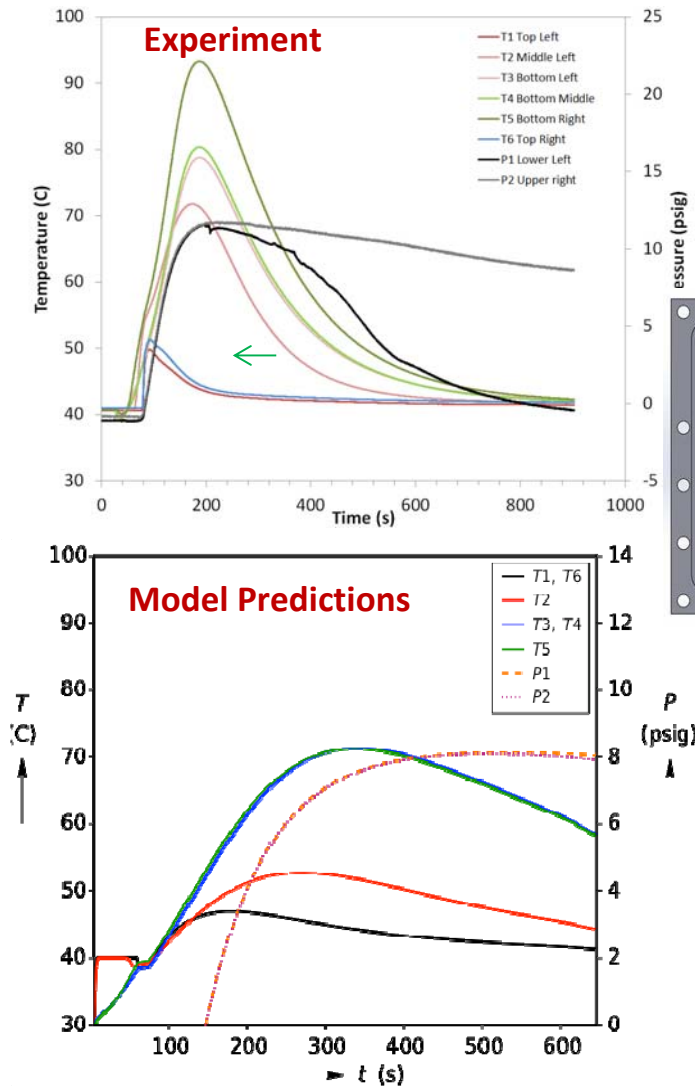
Warpage Measurements

- Components Allowed to cool to room temperature and removed from the mold
- Components stored at room temperature in sealed containers with desiccators
- Coordinate Measurement Machine (CMM by Xzyce)

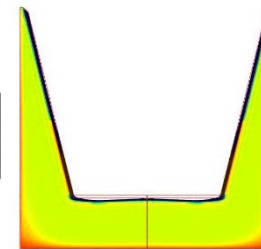


Foaming U-shaped Staple Mold

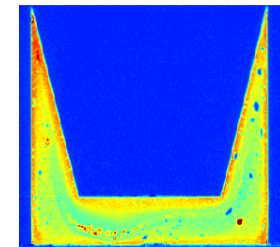
- Over many repeats, temperature, pressure, and flow profile are remarkably repeatable
- Imperfectly symmetric fill common
- Pressure rises as foam expands, relaxes at lower corner and stays positive at P2.



Density
 1.400e+01
 1.300e+01
 1.200e+01
 1.100e+01
 1.000e+01



Model

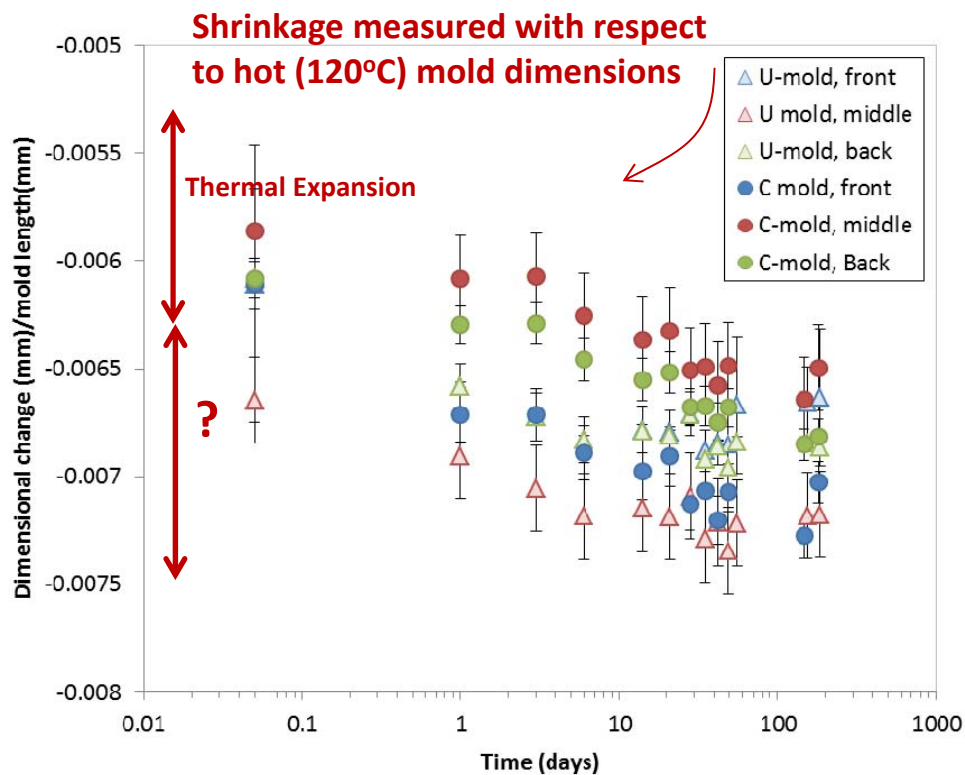


X-ray CT Data
 (Thompson,
 2016)

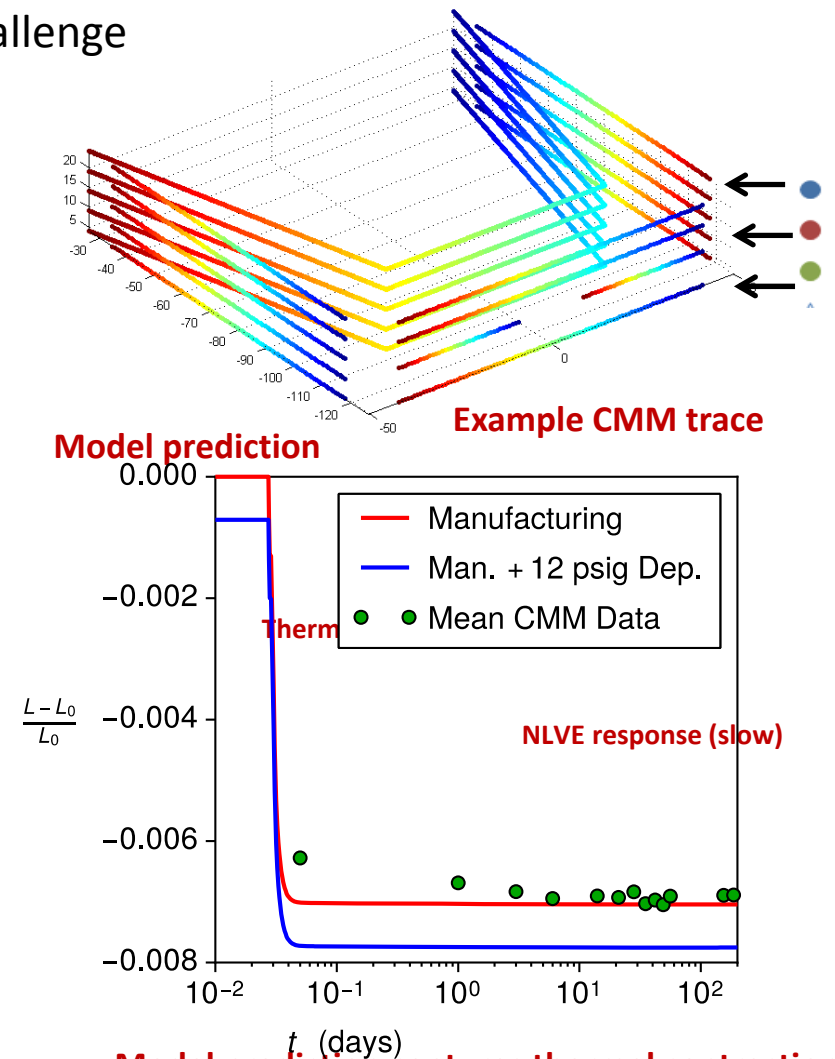
Density
 (lb/ft³)
 25
 20
 15
 10
 5
 0
 -5

Long-Time Shrinkage

- C- and U- shaped staple foam pieces cured 120°C, 4 hours in mold
- Mounted upright, measured using CMM weekly (100 mN probe force)
- All surfaces move in time – defining origin a challenge



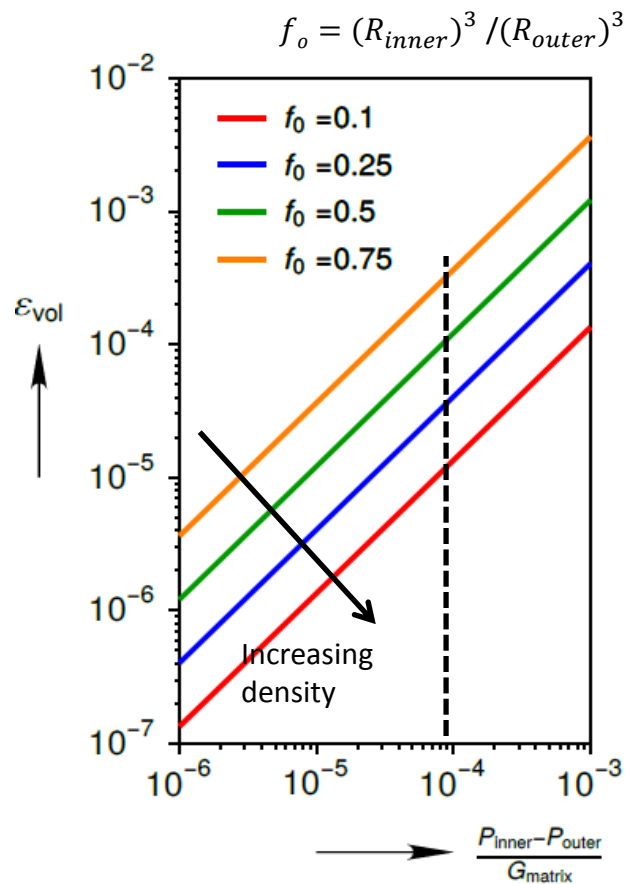
Combination of aging experiment and NLVE modeling elucidate new shrinkage mechanism!



Model prediction captures thermal contraction
Relaxation of residual stress is extremely slow (eons)

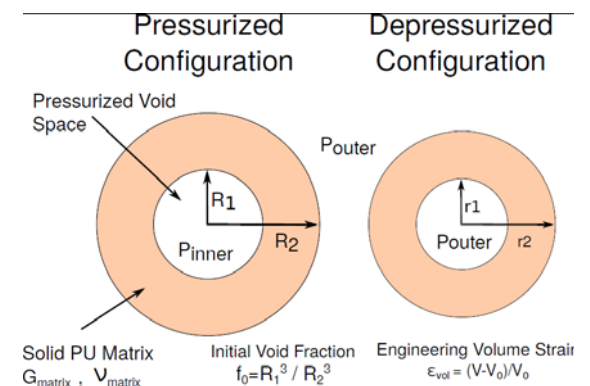
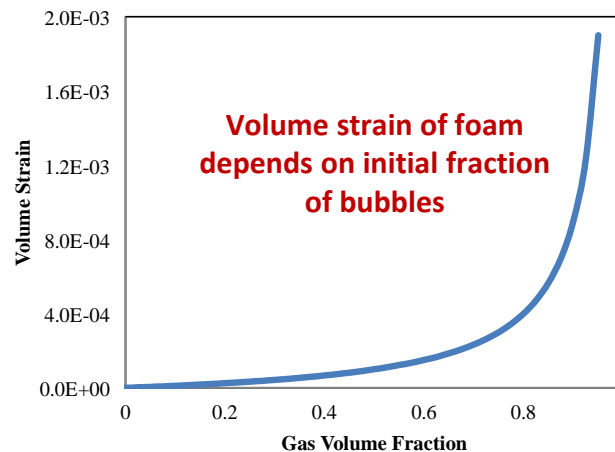
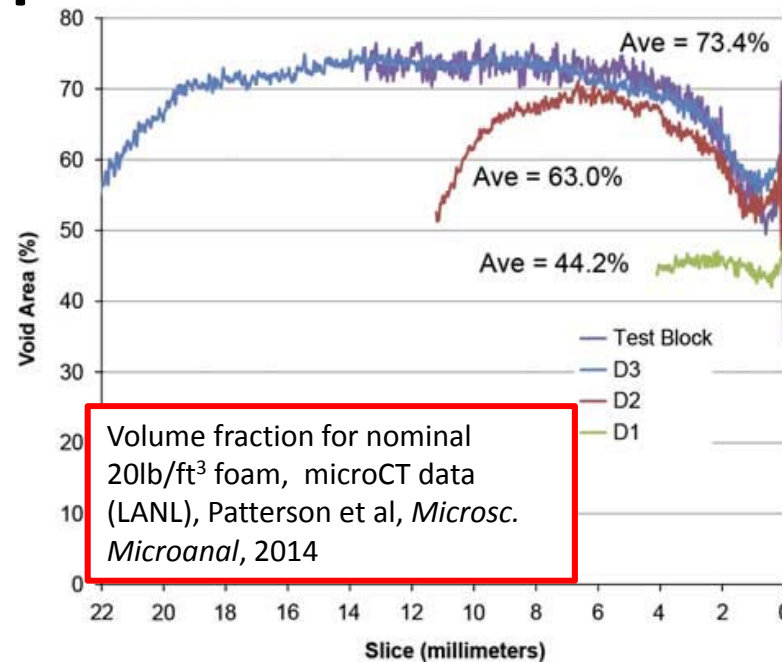
Bubble Depressurization

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



For our foam $\Delta P/G$ is $\sim 1e-4$

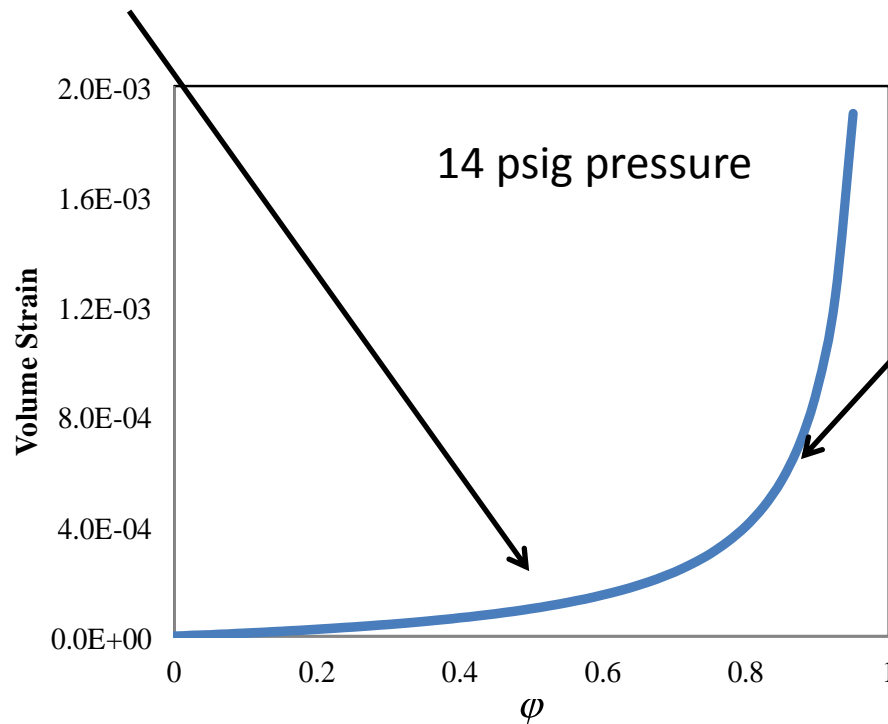
$\nu \sim 0.3$, $G \sim 1\text{GPa}$, $\Delta P \sim 14\text{ psig}$



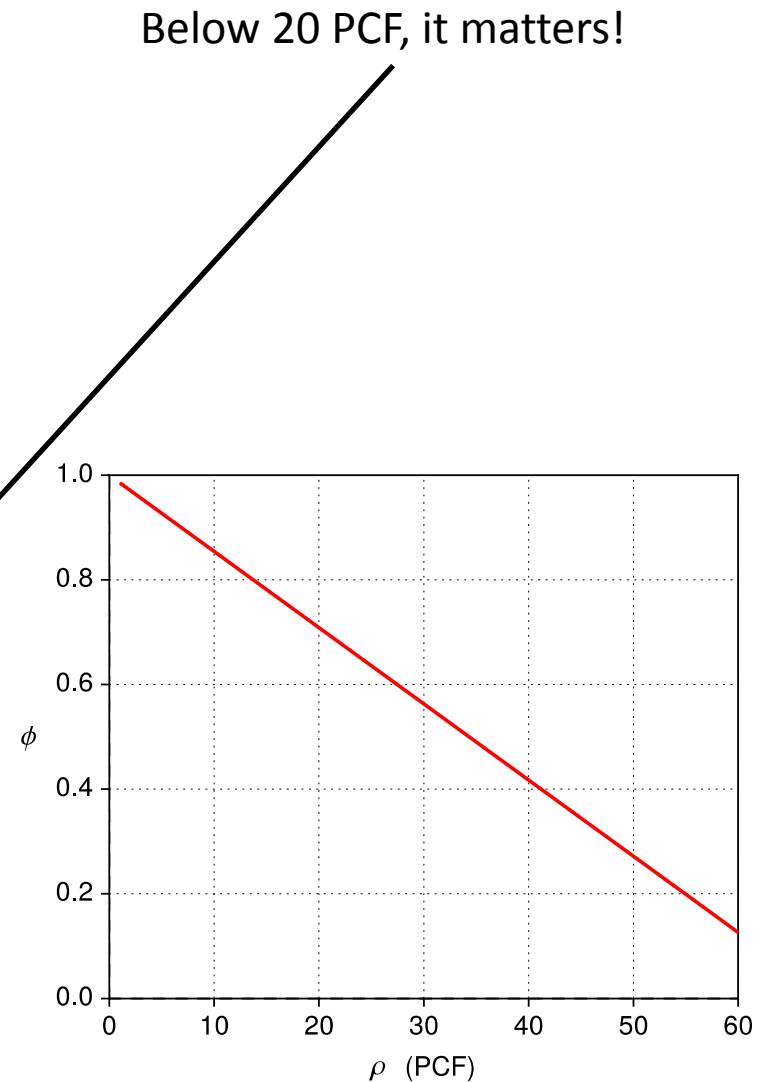
Bubble Depressurization May be Important for Low Density Foams

Originally, we focused on higher density foams: 40, 50, 55 PCF

→ Depressurization strains appear negligible



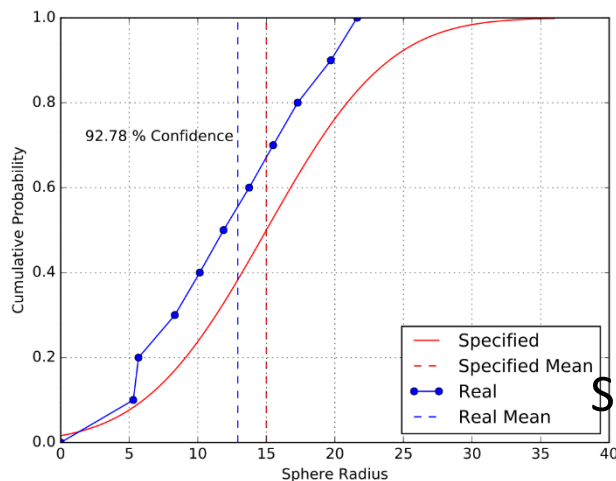
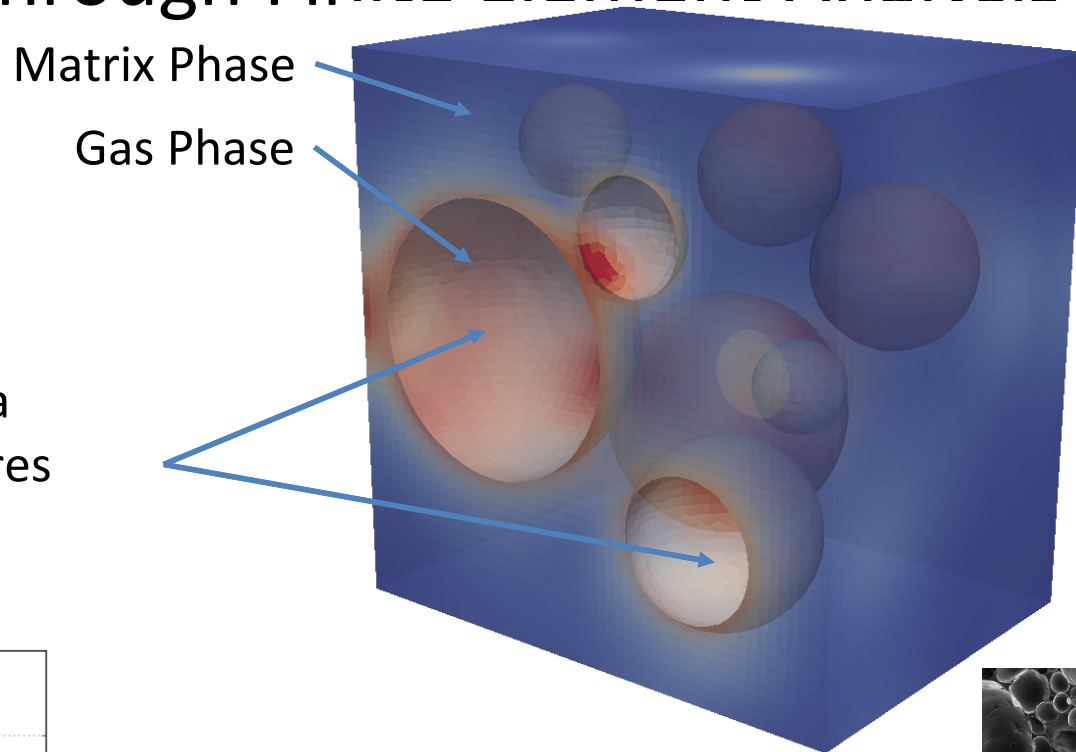
Bubble depressurization matters for smaller foam densities (assuming a fixed gauge pressure...)



How Accurate is the Analytic Model?

Validation Through Finite Element Analysis

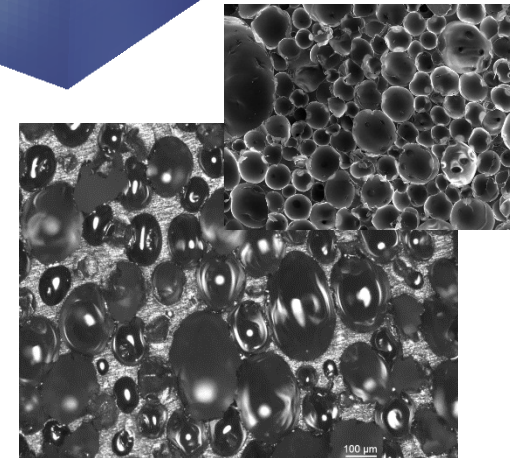
- Prescribed porosity
- Depressurization Over a Range of Gauge Pressures inside to pores



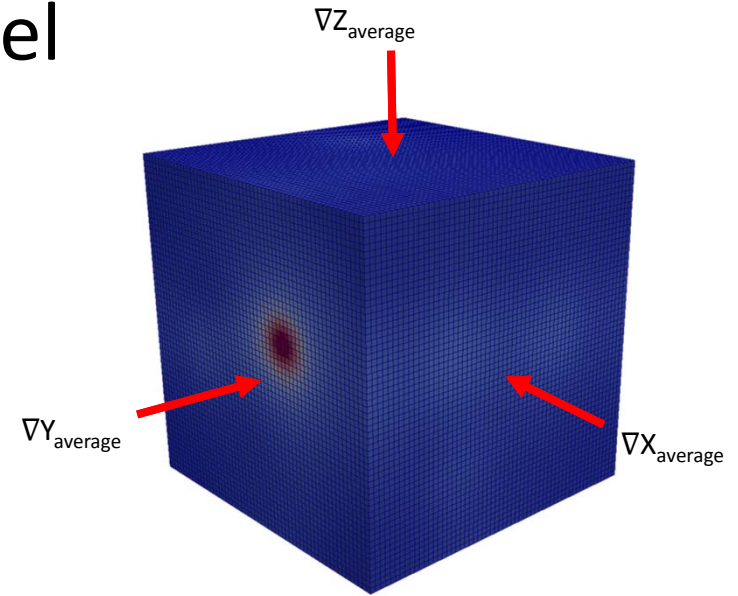
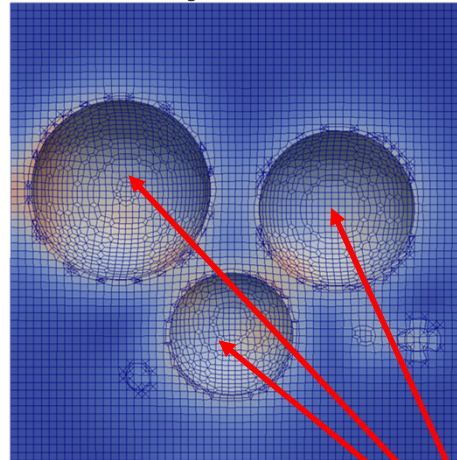
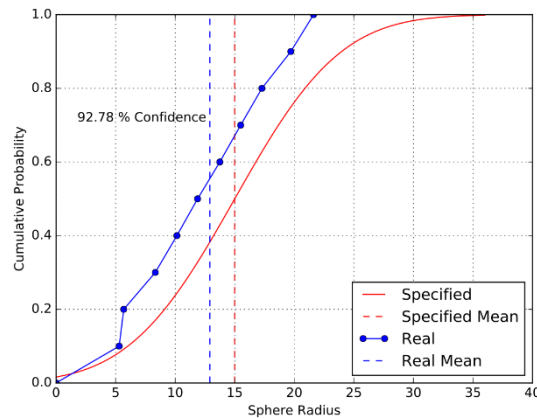
Different size distributions

- Gaussian, Uniform

Spherical voids may be ok over a range of porosities



Micromechanics Validation of the Analytic Model



Pore geometries generated for multiple porosities (Gaussian distribution)



Porous cubes created and meshed



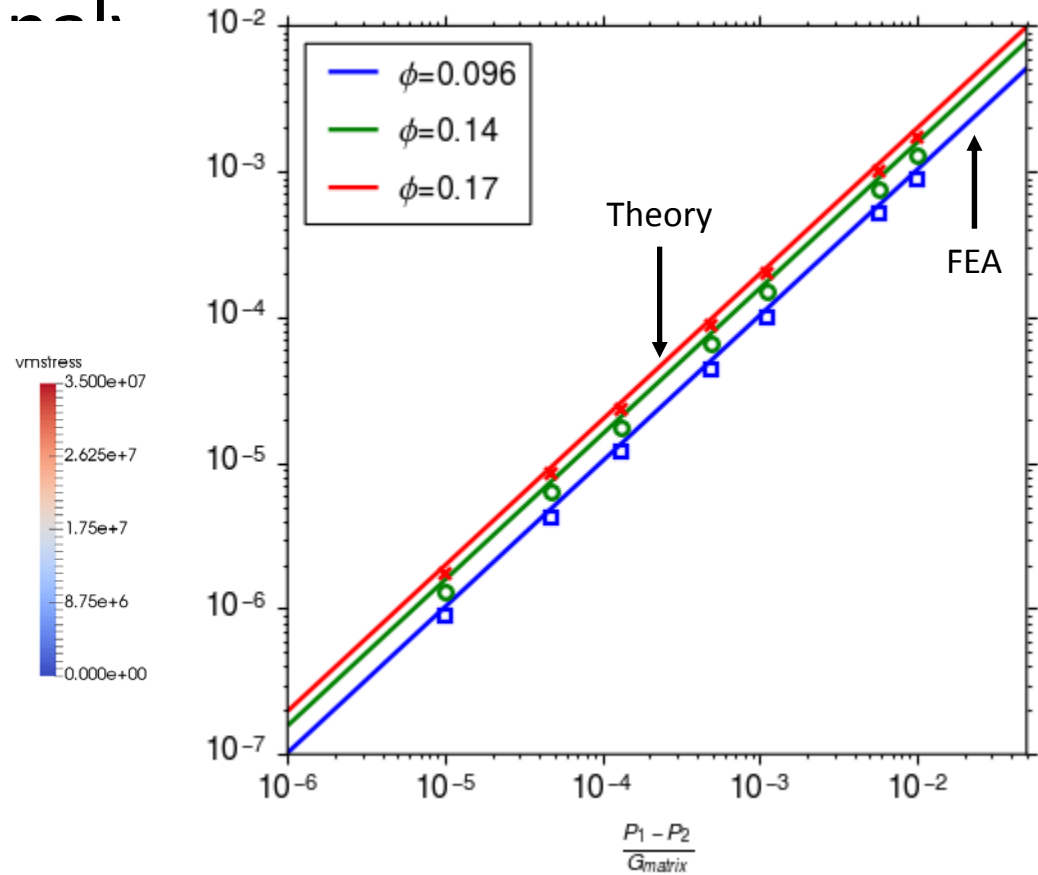
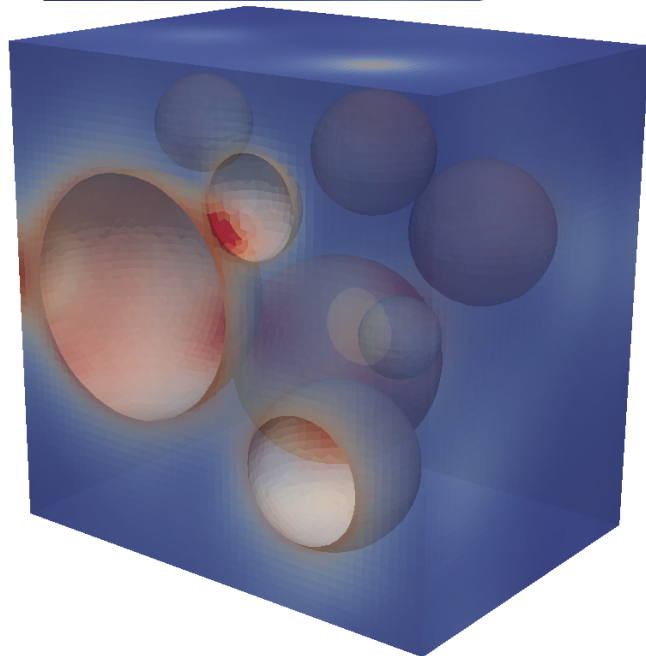
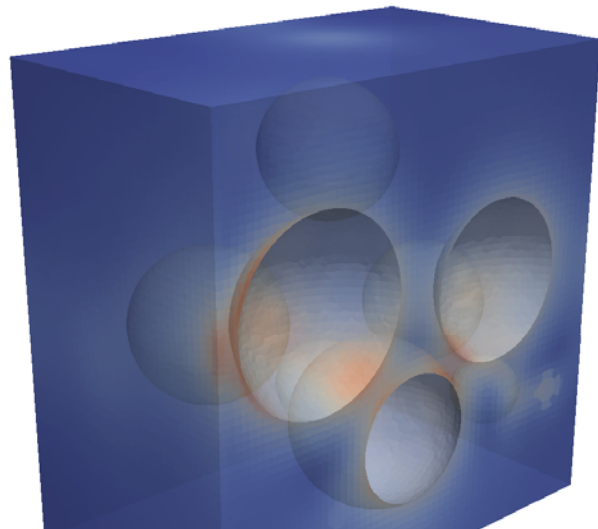
Decreasing gauge pressure applied to pore surfaces



Volume strains calculated

Micromechanics Validation of the

Analysis

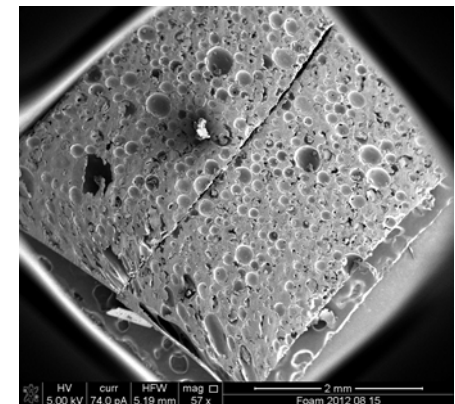
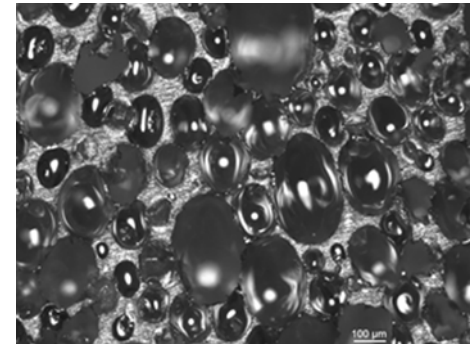


The Analytic Model Reasonably Well Represents Deformation Due to Depressurization for Isotropic Foams at least at Low Porosities

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

SEM of foam
showing
polydispersity



Bubble at walls are
elongated and show
coarsening