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Continuum Modeling and Flow Visualization of Blown Foams

Rekha Rao, Lisa Mondy, Jeremy Lechman,Doug Adolf,
Thomas Baer, Edward Russick, Andy Kraynik
Sandia National Laboratories, Albuquerque, NM

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
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Goal: To Understand Manufacturing of Blown Epoxy Foam

Motivation

- Foams are ubiquitous in the manufacturing sector but still poorly understood
- Foams are used for insulation, shock, and vibration isolation
- Foams are complex, multicomponent, reacting materials
- Fundamental understanding of foam processes can allow us to manufacture better foams (without density and modulus variations)

Approach

- Coupled Computational Modeling
  - Model development closely linked to experimental work
  - Kinetics
  - Rheology
  - Blowing agent transport
  - Thermal modeling
  - Fluid mechanics
  - Microscale and mesoscale modeling
  - Validation experiments

Foams can show density gradients top to bottom, areas of large irregular bubbles, and wall (skin) effects

Foam of Interest is Physically Blown

Vision: Develop a continuum model with volume source terms, and include relevant physics in these terms.

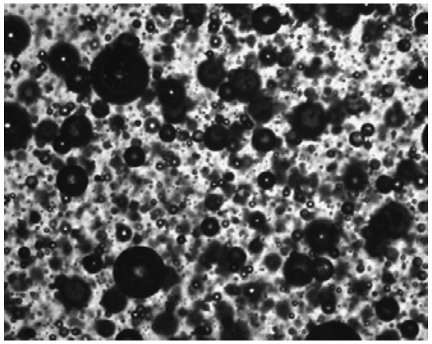
Process

- Two part epoxy, starts as an emulsion
  - Part B (shaken to distribute components)
    - Cabosil M-5 (particulate for nucleation sites)
    - curing agent
    - surfactant
    - FC-72 Fluorinert (blowing agent
      ring
  - resin
- Fo
  - ls at 53ºC)

What we need to know

- Reaction kinetics, thermal properties, rheology of continuous phase, etc
- Nucleation mechanism
- Growth stage physics
  - How much blowing agent is used and how much lost?
  - Emulsion/foam microstructure
- Foam properties
  - Heat transfer & rheology
  - Density & bubble size
  - Wetting/slip at walls

Bubbles in a soft drink nucleate homogenously, responding to a decrease in pressure



Epoxy foam starts out as an emulsion and probably nucleates heterogeneously

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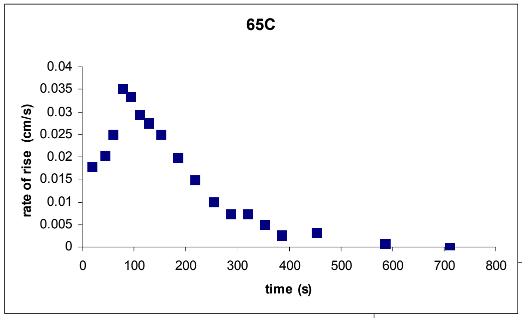
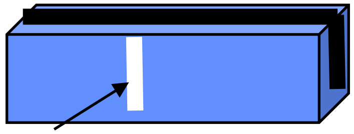
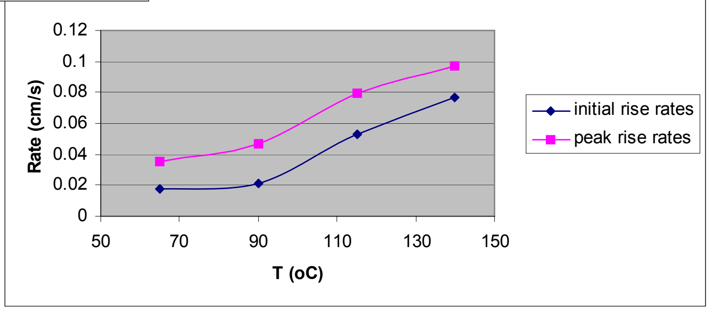
Foam Rise Experiments

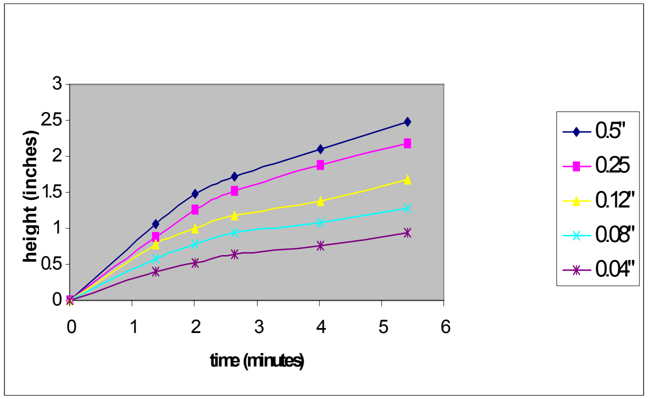
- Foam expansion in narrow (1/4”) slots
- Foam rise velocity increases over first minute or so, then decreases because gas is used up and/or viscosity of polymerizing resin increases
- Rise rate is dependent on temperature
- Rise rate is dependent on channel size in simple geometry
- Interplay of these effects in a complex geometry not obvious without modeling (see next slide)





Viewing window





Foam Rise Experiments in More Complex Geometry

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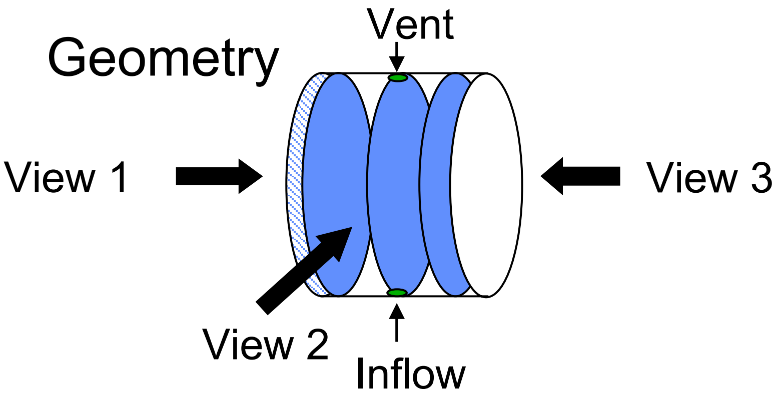
FOAM RUN # 4
EFAR 08
Oven 54 Foam 54
Oven cure temp 54

4/12/06



Geometry

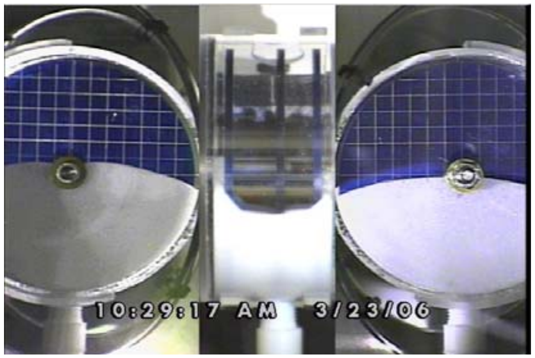
Vent

View 1

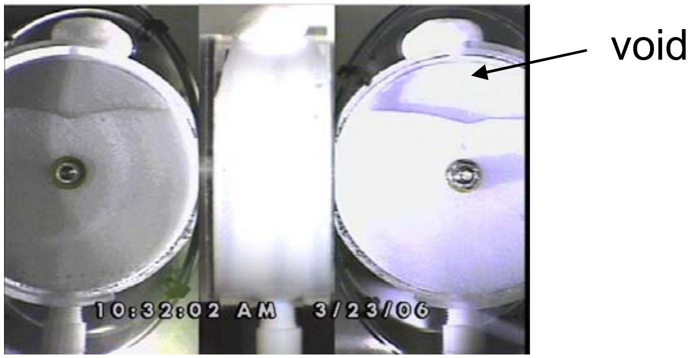
View 3

View 2

Inflow



Early: unlike in simple geometry experiments, epoxy foam (EF-AR08) fills *faster* in the *narrow* gaps between plates.



A few minutes later: foam speeds up in the big gaps and slows in the narrow ones.

Heat transfer from oven critical.
Competing effects → models needed.

Proposed Continuum Blown Foam Model

Seo and Youn, Polymer, 2005; Marciano et al., Poly. Eng. Sci, 1986;

Momentum equation:

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

Dilatational viscosity, $\lambda = \frac{4}{3}\mu_0 \frac{(\phi_0 - \phi - 1)}{\phi_0 - \phi}$

$$\nabla \bullet \mathbf{v} = -\frac{1}{\rho_f}\left(\frac{\partial \rho_f}{\partial t} + \mathbf{v} \bullet \nabla \rho_f\right)$$

Continuity equation:

$$\frac{\partial(\rho_f C_{pf} T)}{\partial t} + v \bullet \nabla(\rho_f C_{pf} T) + \rho_f C_{pf} T(\nabla \bullet v) = \nabla \bullet (k_f \nabla T) + \rho_f (1-\phi)\Delta H_{rxn} \frac{\partial \xi}{\partial t} - \rho_f \lambda_{evap} \frac{\partial \phi}{\partial t}$$

Energy equation:

$$\frac{\partial \xi}{\partial t} + \nabla \bullet (\xi v) = k^i e^{\Delta E / RT} \left(1 - \xi\right)^n$$

Proposed Blown Foam Model

- **Liquid phase volume fraction of blowing agent: equilibrium model**

$$\frac{\partial x}{\partial t} = \left(\frac{\partial x}{\partial T}\right)_{\exp} \frac{\partial T}{\partial t} \qquad T \geq T_{boiling} \qquad\qquad \phi = \frac{\rho_f}{\rho_{fluorinert}} x_{fluorinert}$$

- **Density equation:**

$$\rho_f = [(x_0 - x)\frac{RT}{pM} + (1 - x_0)\frac{1}{\rho_{epoxy}} + \frac{x}{\rho_{flourinert}}]^{-1}$$

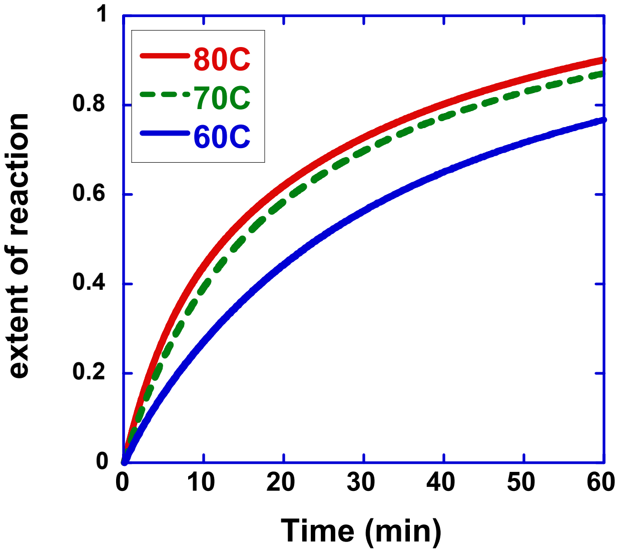
- **Viscosity equation:**

$$\mu = \mu_0 \exp\left(\frac{\phi_0 - \phi}{1 - \phi_0 + \phi}\right), where \mu_0 = \mu_0^0 \exp\left(\frac{E_\mu}{RT}\right)\left(\frac{\xi_c{}^2 - \xi^2}{\xi_c^2}\right)^{-4/3} \qquad \xi_c = 0.45$$

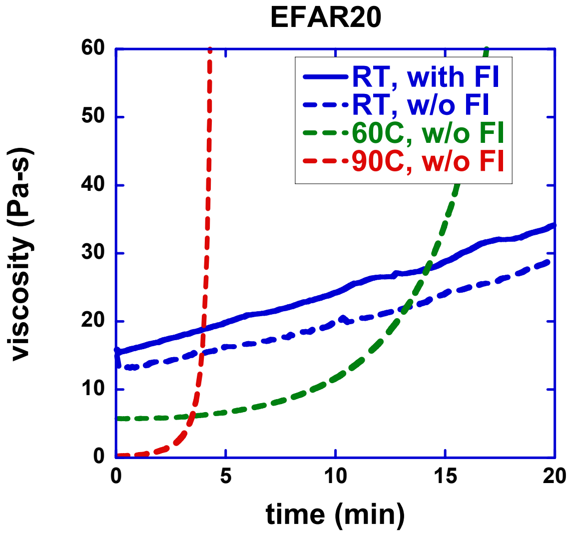
Reaction Kinetics and Rheology for Continuous Phase Determined Experimentally

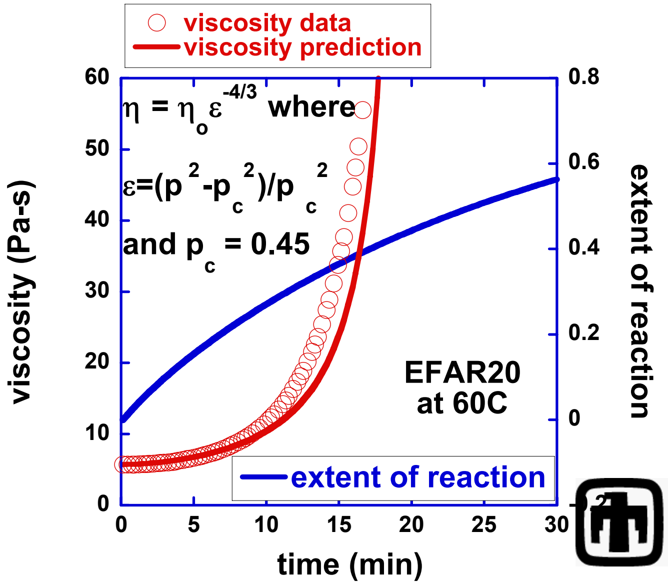
- Reaction kinetics for foam determined by differential scanning calorimetry
- Polymerization of epoxy material follows condensation chemistry
- Reaction is exothermic (ΔH_{rxn} = 250 J/g)
- Heat produced drives the reaction faster
- k=1.145e5 ΔE=10kcal/mol, n=1.3

$$\frac{d\xi}{dt} = ke^{\Delta E/RT}(1-\xi)^n$$



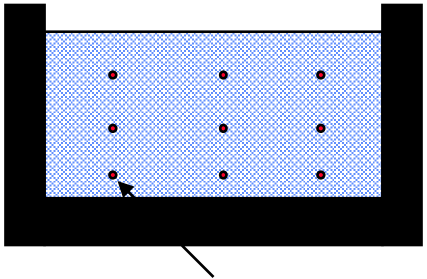
- Viscosity increases with cure
- Correlate viscosity with extent of reaction





Foam Rise Experiment Offers Guidance for Manufacturing as well as Validation for Models

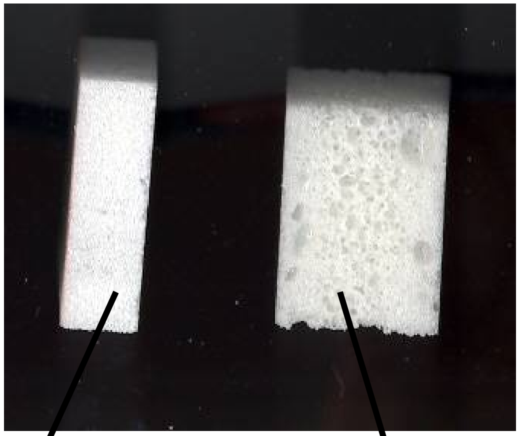
Schematic of Experiment



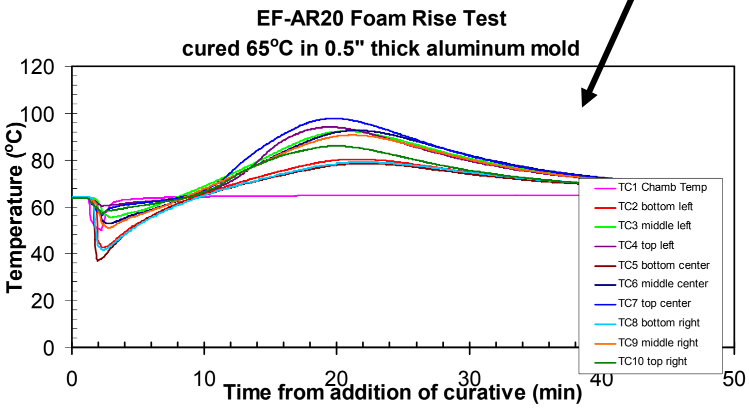
Thermocouples

Vary thickness (out of the plane of the paper)

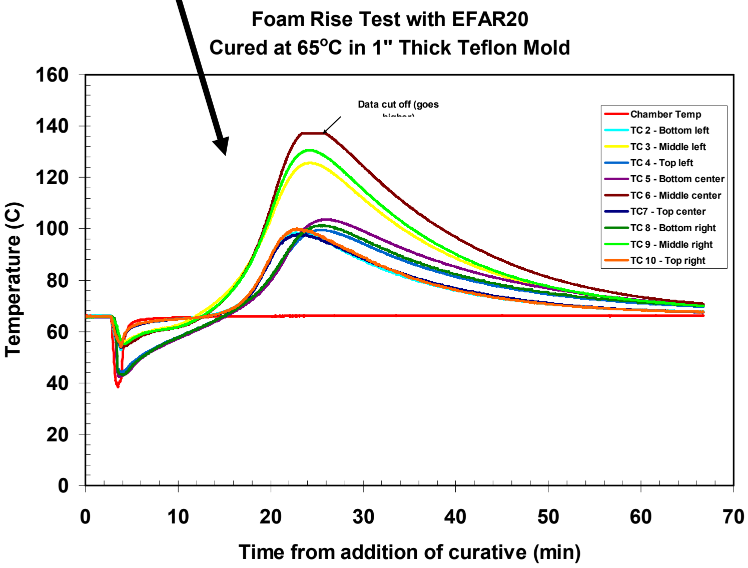
Photo of cured foam section from middle
Left ½ inch thick, Right 1 inch thick



- Thicker sections exotherm and produce coarser, lower density, more nonuniform foams

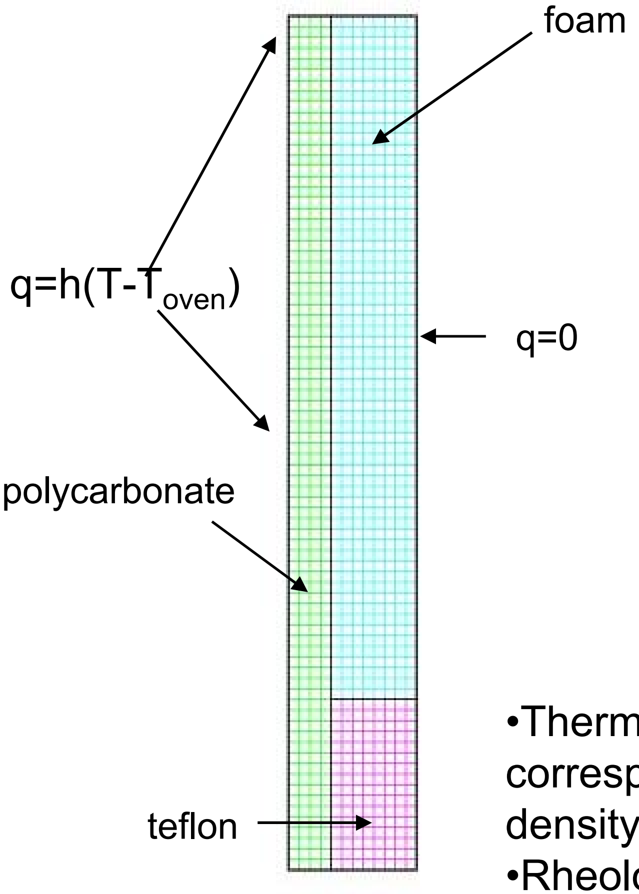


EF-AR20 Foam Rise Test
cured 65°C in 0.5" thick aluminum mold



Foam Rise Test with EFAR20
Cured at 65°C in 1" Thick Teflon Mold

Foam Thermal Simulations Can Give Insights Into “Hot Spots” in 1 inch Foam Experiments



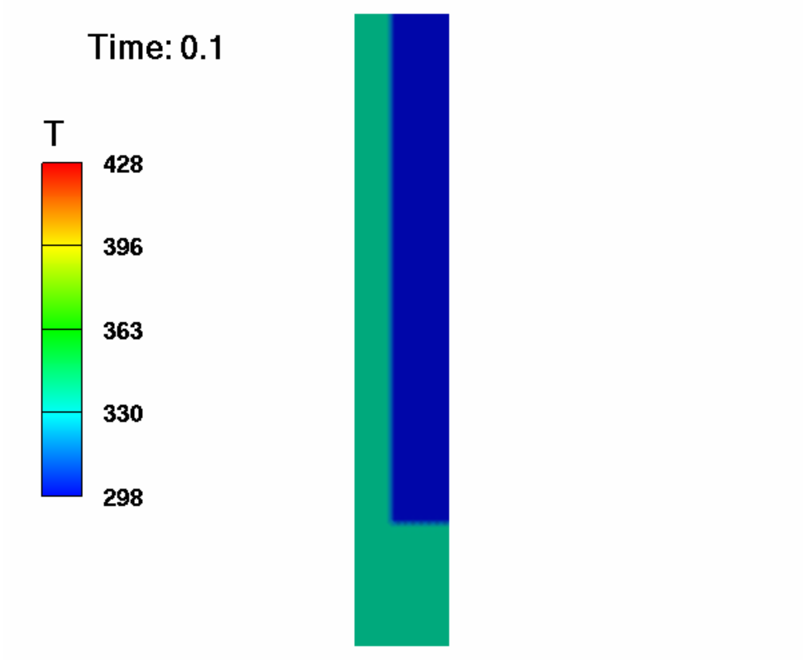
foam

$q=h(T-T_{oven})$

q=0

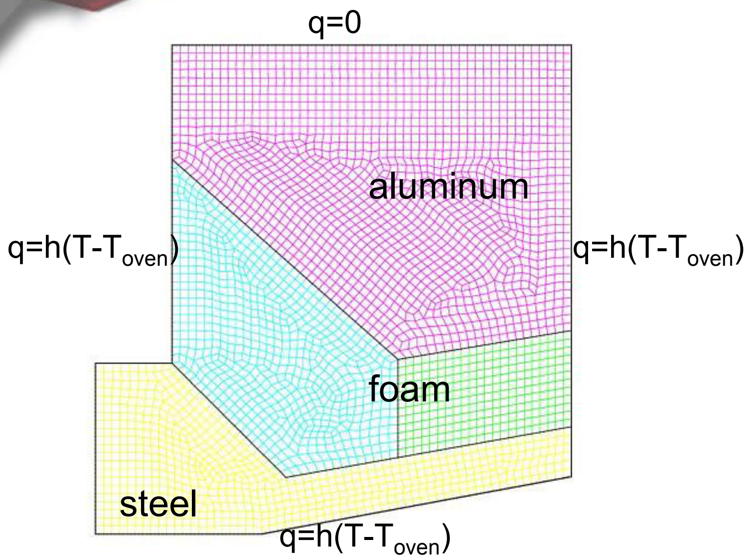
polycarbonate

teflon

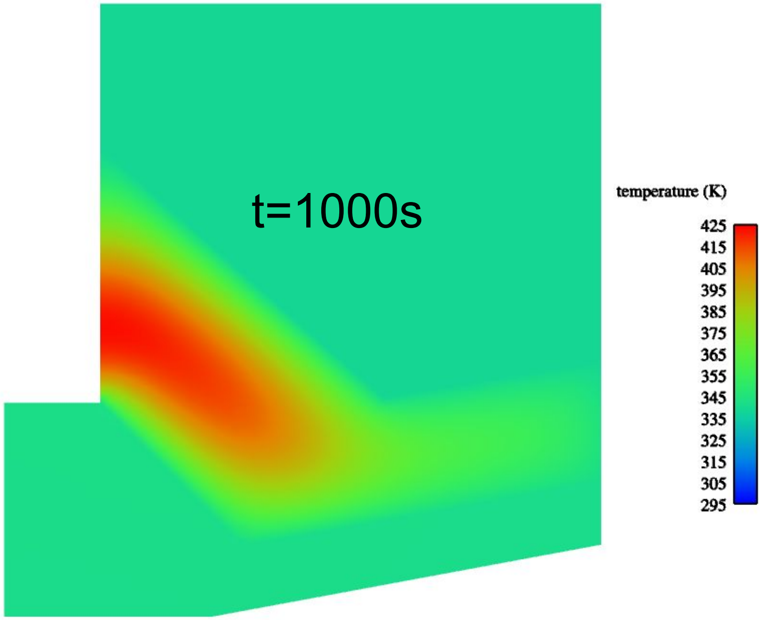


- •Thermal analysis predicts hot spots that correspond to regions of large bubbles and low density in the experiment
- •Rheological model must be nonisothermal and take into account the effect of temperature on bubble growth

Thermal Analysis Of Foam Reaction



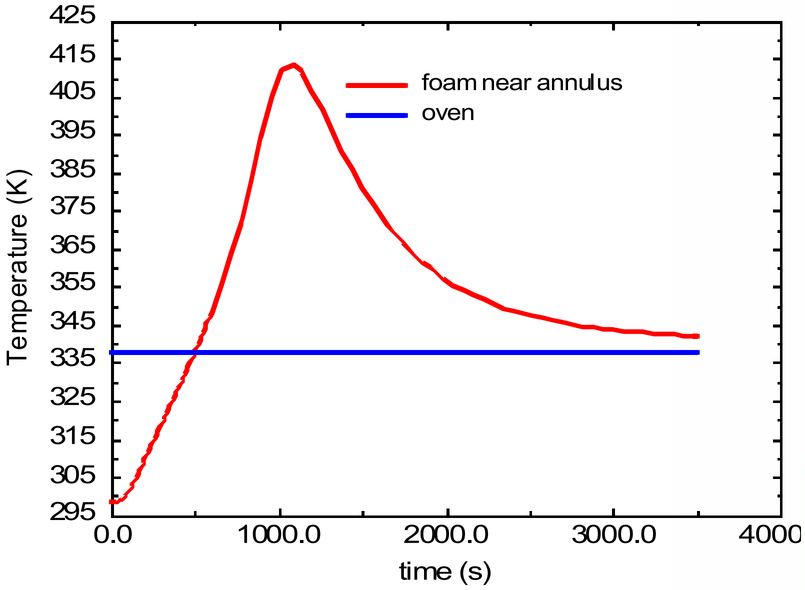
Axisymmetric mesh



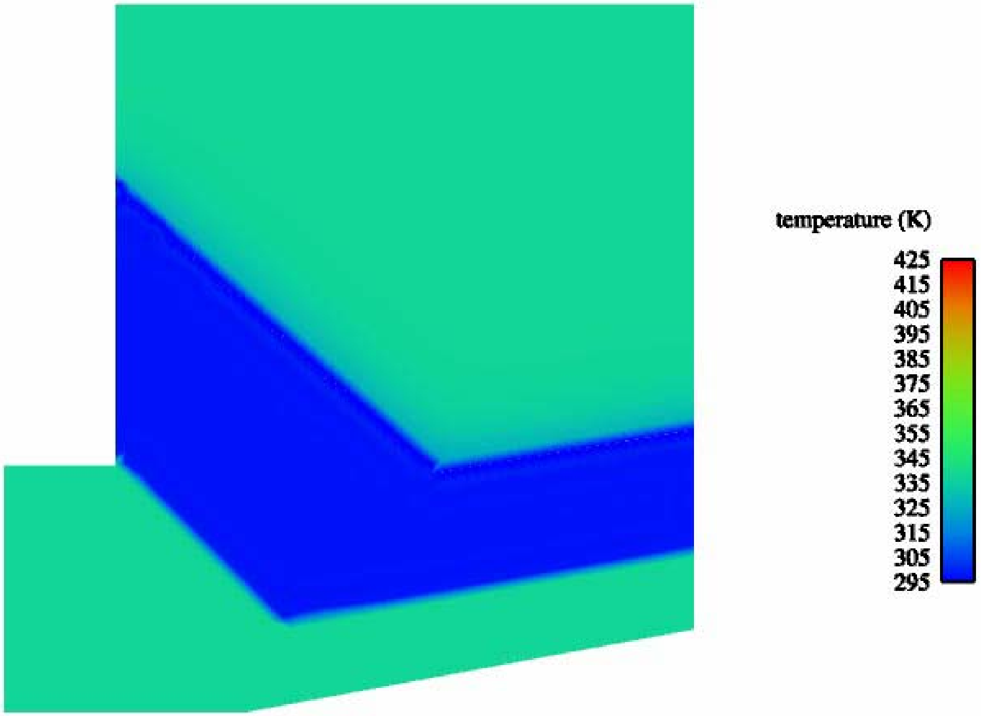
Foam temperature after 1000s

- •Transient thermal analysis with reaction kinetics show significant exotherm
- •Foam heats up 80^{o}C higher than oven temperature
- •Highest temperatures are seen 18 minutes after insertion into oven
- •Experiment shows large bubbles in hottest regions

Temperature Variations Over Time For Thermal Analysis Of Foam Reaction



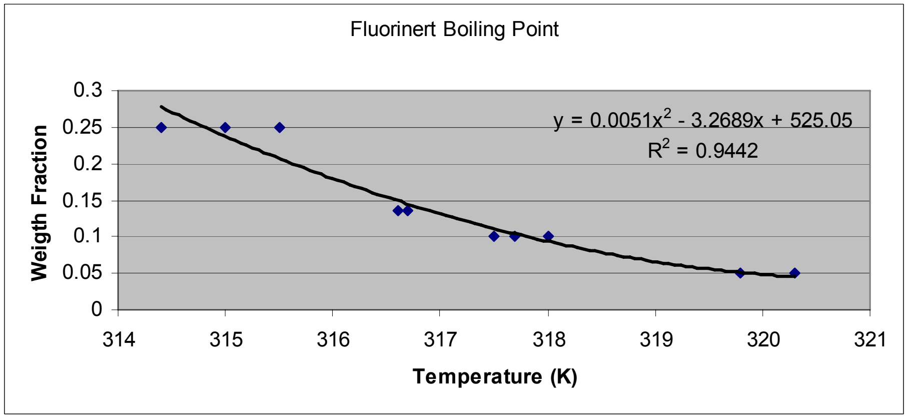
Foam temperature near annulus plotted with the oven temperature



- Foam initially at room temperature and is inserted into a mold preheated to the oven temperature
- Foam heats up to oven temperature, exotherms, and cools back down to oven temperature

Fluorinert Vaporization Model

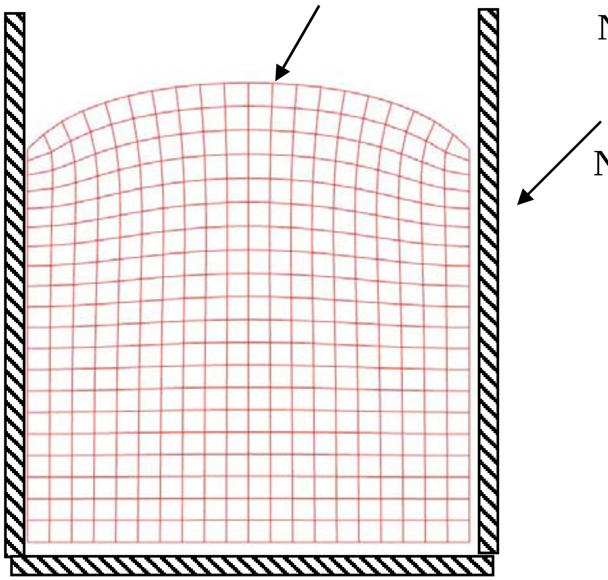
- Boiling point experiments
  - If liquids mixed so that there were no air bubbles then it would superheat and then violently foam if triggered
  - If shaken so bubbles entrained, then foamed evenly



- Air seems necessary for foaming to occur
- Slow "take off"
- Foaming starts below boiling point of liquid foaming agent

$$\frac{\partial x}{\partial t} = \left(\frac{\partial x}{\partial T}\right)_{\exp} \frac{\partial T}{\partial t} \qquad T \geq T_{boiling}$$

Simple Foam Rise in Between Flat Plates



Kinematic condition at the free surface

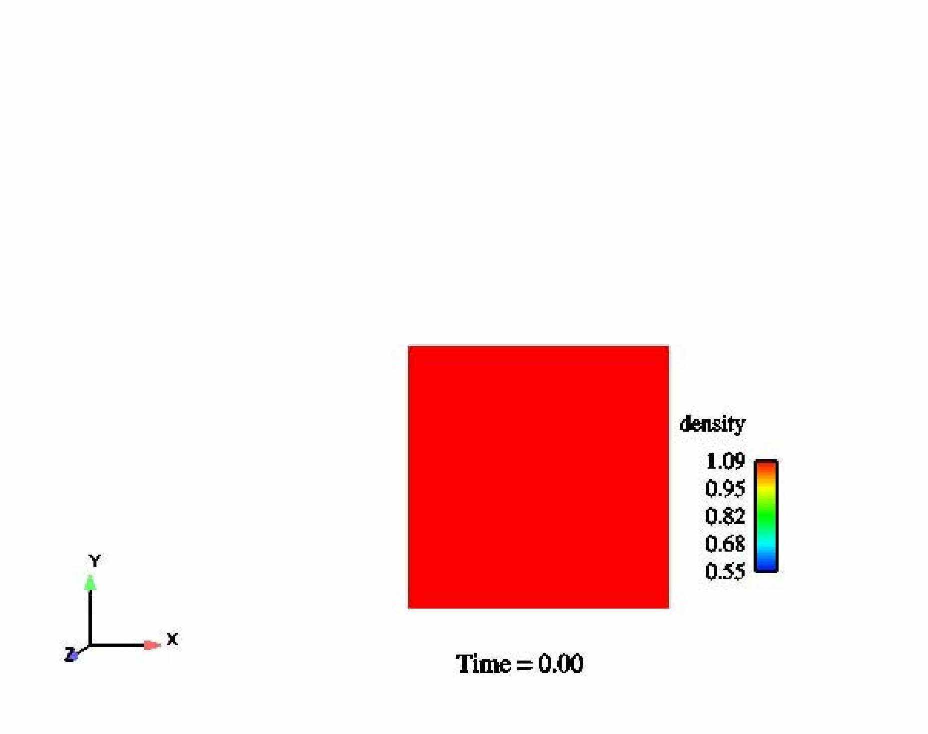
$$n_{fs} \bullet (v - \dot{X}) = 0$$

No penetration

$$u_{normal} = 0$$

Navier slip condition

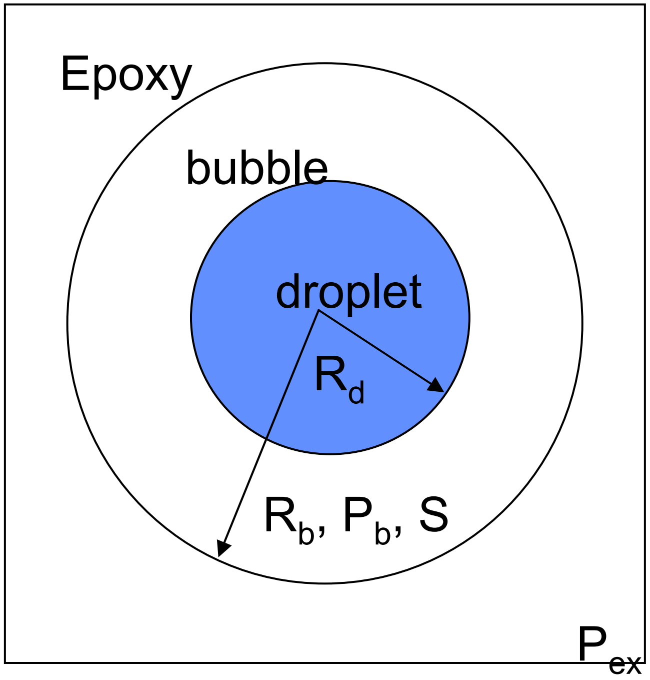
$$n \bullet \tau_{slip} = \frac{1}{\beta} u_{\tan gential}$$



- Moving mesh algorithm to handle moving boundary problem
- Coupled fluid mechanics, mass, energy transport, kinetics
- Coupling creates a stiff problem
- Current fluorinert blowing model behaves poorly for large temperature gradients
- Density model cannot handle fluorinert gradients

Microscale Foam Expansion Model

- **Idea: Droplet evaporating inside a bubble expanding in an infinite Newtonian viscous fluid**
- **Assume:**
  - **homogeneous T (ignore heat gain/loss of droplet)**
  - **gas/vapor is ideal**
  - **ignore fluid inertia (** $Re = \sigma/(2\mu) * \sqrt{\rho / P_{ex}} \sim 10^{-4}$ **)**
- **Driving mechanism: initial droplet bigger than equilibrium size with vapor (Kelvin relation)**



$$R_d = \frac{v_m \sigma_{db}}{R_G T \ln S}; \quad S = P_b / P_{sat} \qquad [1]$$

Where v_m is the molecular volume, R_G gas constant, σ_{db} surface tension, P_{sat} vapor pressure at coexistance for a planar interface

  - **For typical materials S < 0.99 gives $R_d \sim O(1 - 100\text{nm})$**
  - **Experimentally, $R_d \sim 10\text{-}100\mu\text{m}$**
  - **Therefore, droplet will evaporate**

Rates of Droplet Evaporation and Bubble Expansion

- As the bubble evaporates the steady-state rate of mass transport away from its surface is given by

$$D\frac{dN}{dr} = \frac{\dot{m}_d}{A_d} \quad [2]$$

where *D* is the diffusion coefficient, *N* number density of vapor, A_d surface area of the droplet

- Also, continuity gives

$$\dot{m}_d = \rho_d \frac{dV_d}{dr}\frac{dR_d}{dt} \qquad [3]$$

where V_d is the volume of the droplet

- Integrating [2] and substituting [1] and [3] yields

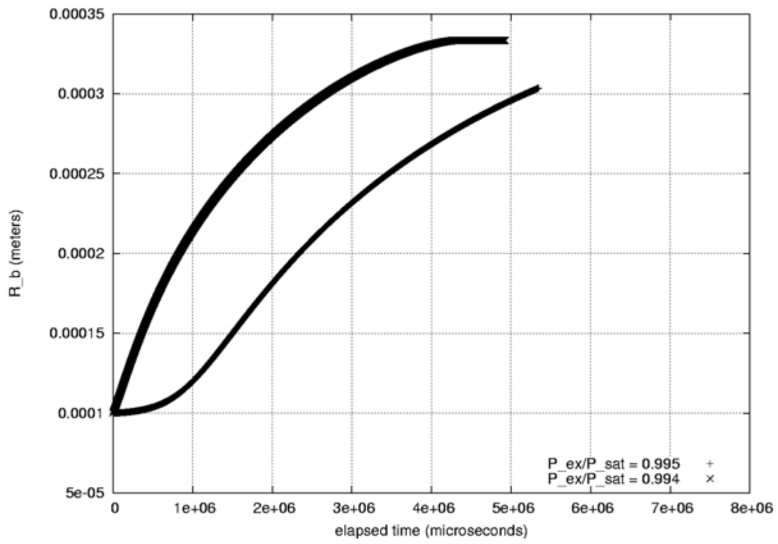
$$\frac{dR_d}{dt} = \frac{DM_d P_{sat}}{R_G T \rho_d}\left(\frac{1}{2R_d}\right)\left[S - \exp(-\sigma_{db} v_m / k_B T R_d)\right]$$

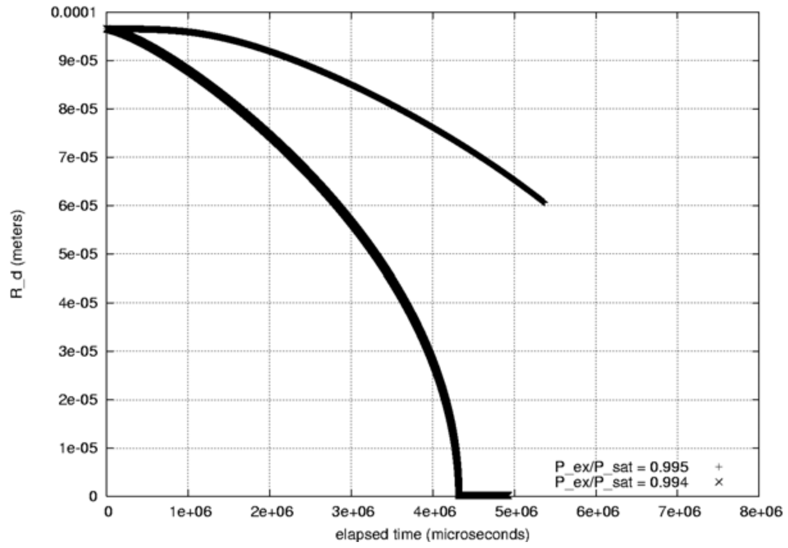
- Rate of bubble expansion: $\frac{dR_b}{dt} = (P_b - P_{ex})R_b - 2\sigma_{db}$

See, for example, Scriven (1959) *Chem Eng Sci*,vol 10, pp 1-12. Barlow and Langlois (1962) *IBM Journal*, July, pp 329-337.

A Small Change in P_{ex}/P_{sat} Changes Expansion Time

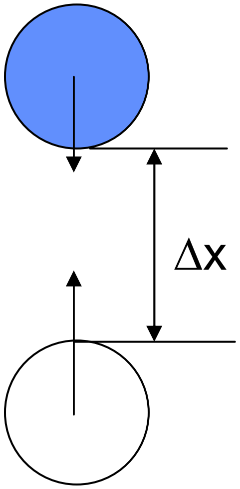
- Numerical implementation with simple Euler scheme and “time-lag coupling” between droplet and bubble (i.e., evaporate drop for Δt, then expand bubble for Δt and repeat)
- $T = 35°C$, $S = 0.995$, $R_b(0) = 100\mu m$, $R_d(0) = 96.5\mu m$, $R_d^{eq} = 189nm$
- Note: $P_{ex} \sim 3.0*P_{atm}$
- 0.16% change in P_{ex}/P_{sat} can have a factor of ~2 change in the bubble expansion time
- Expansion time is several seconds



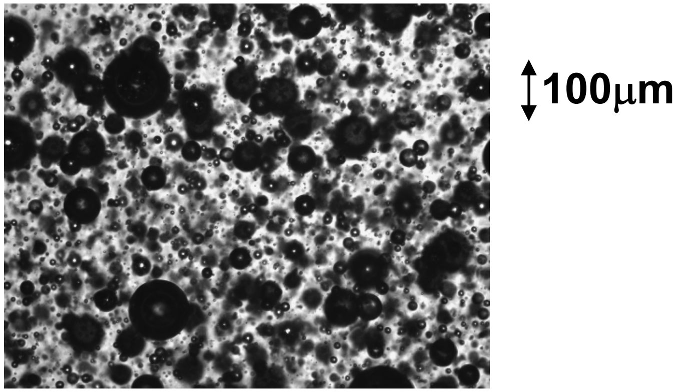


To Get Expansion Time on Order of Minutes: Nucleation Limited

- Assuming a bubble rising and a droplet sedimenting at their respective terminal Stokes velocities and $R_d = R_b \sim 100\mu m$ gives an average collision time on the order of minutes if Δx is on the order of $100\mu m$



$$v_{S,i} = \frac{2R_i^2 g}{\nu_f}\left(\frac{\rho_i}{\rho_f} - 1\right)$$



Conclusions and Future Work

- **Foams are complex, poorly understood, materials**
- **Coupled physics requires modeling**
  - **Preliminary modeling shows areas for improvements in density and fluorinert vaporization model**
  - **Micro- and meso-scale modeling will be used to develop continuum foam expansion model and boundary conditions**
- **Experimental discovery and multiscale modeling used to develop continuum model for blown foams**
  - **NMR and confocal for droplet size**
  - **Initially we will use a description of the cell size evolution determined by mass transport from blowing agent droplets**
  - **Effects of temperature will be added to this basic model**