Caltech

In collaboration with the University of Naples Federico II

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For Polyurethane Foam, "More" Means "Less":
Adding "C5" Dramatically Reduces Nucleation Barrier of CO_2

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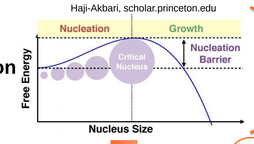
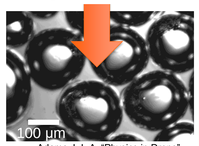
Polymer Foams Undergo 3 Stages: Nucleation is Least Understood

1. Nucleation



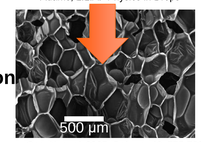
Nucleation is most difficult to measure
- Stochastic
- Occurs in milliseconds
- Nanometer length scales

2. Growth & Coalescence



Adams, L.L.A. "Physics in Drops"

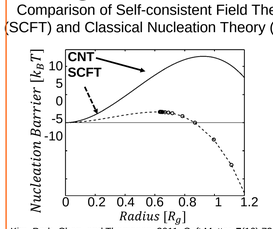
3. Solidification



Cao, X. *et al.* 2005, *Polymer* **46**, 775-783

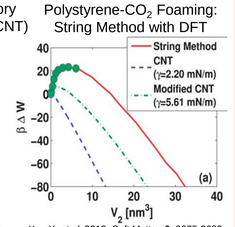
Disagreement in Theoretical Models

Comparison of Self-consistent Field Theory (SCFT) and Classical Nucleation Theory (CNT)



Kim, Park, Chen, and Thompson, 2011, *Soft Matter*, **7**(16):7351

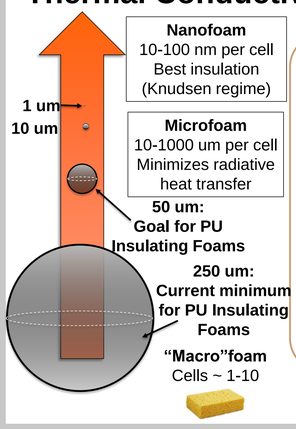
Polystyrene-CO_2 Foaming: String Method with DFT



Xu , X. *et al.* 2013, *Soft Matter*, **9**, 9675-9683

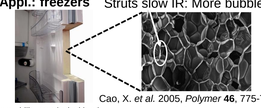
*Different methods predict **vastly different** nucleation energy barriers ΔW (and nucleation rate $\propto e^{\Delta W/k_BT}$), but experiments to validate them are lacking*

Increasing Bubble Nucleation Important to Reduce Thermal Conductivity of Polyurethane Insulating Foams



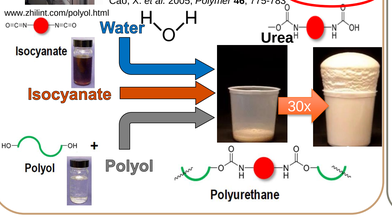
Polyurethane Foaming Reaction

Appl.: freezers — Struts slow IR: More bubbles = more struts

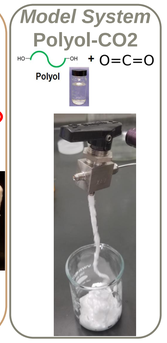


Cao, X. *et al.* 2005, *Polymer* **46**, 775-783

CO2 drives much of foam expansion



Model System Polyol-CO_2



Still makes a reasonable foam!

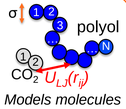
Modeling of Bubble Nucleation Requires Equilibrium and Interfacial Properties

PC-SAFT and other model development performed by Dr. Huikuan Chao @ Caltech

Equilibrium Behavior: ***PC-SAFT*** → Pass Parameters → Interfacial Properties: ***DFT*** → Calculate Energy Landscape → Nucleation: *String Method*

CO_2-rich / Polyol-rich

Assumes homogeneous phases in equilibrium



Models molecules as chains of beads with Lennard-Jones interactions

$$U_{LJ}(r_{ij}) = -\epsilon_{ij}\frac{\sigma_{ij}^6}{r_{ij}^6}, (r_{ij} > \sigma_{ij})$$

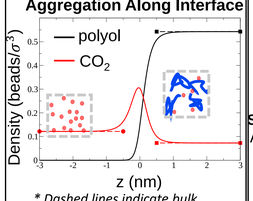
$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}(1 - k_{ij}), (i \neq j)$$

Empirical Parameters
N_i = beads per chain
σ_i =bead diameter
ϵ_i = energy parameter
$k_{ij} = a_{ij}T + b_{ij}$ energy modification for beads of different chemical species

J. Gross & G. Sadowski, Ind. Eng. Chem. Res. **2001**
X. Xu, *et al.*, JCP **2012**

Interface { Phase 1 / Phase 2

DFT Predicts CO_2 Aggregation Along Interface

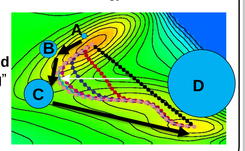


** Dashed lines indicate bulk densities from PC-SAFT calculations*

Parent Phase → Nucleating Phase

The string method calculates the energy landscape as a bubble grows based on DFT, then perturbs the nucleation pathway to find the lowest energy barrier

Schematic Diagram of String Method Adjust "String" to Minimize Nucleation Barrier



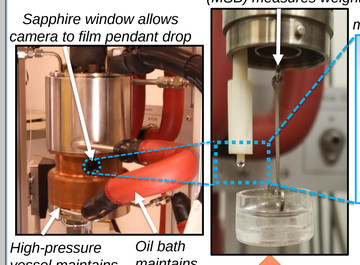
Alberto Giacomello et al. PNAS 2016;113:3:E262-E271

Measure Solubility and Specific Volume to Fit PC-SAFT Material Parameters Using Gravimetry-Axisymmetric Drop-shape Analysis (G-ADSA)

Apparatus

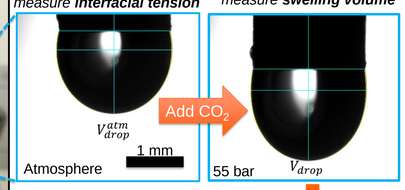
Sapphire window allows camera to film pendant drop

Magnetic Suspension Balance (MSB) measures weight



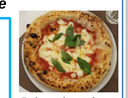
*Pendant drop is used to measure **interfacial tension***

*CO_2 swells polyol drop, measure **swelling volume***



*Swelling volume is used to calculate buoyancy correction to MSB to estimate **density, solubility, and diffusivity***

Buoyancy correction to weight from CO_2
$= \rho_{CO2}(V_{sample,0} + \boldsymbol{V_{swell}} + V_{crucible})$



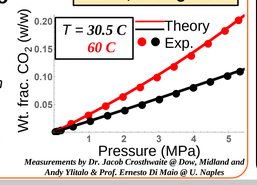
Polyurethane foam is not too different from the crust of a pizza, a Neapolitan creation and classic (Ciro Cascella, Naples, Italy)

G-ADSA developed by Prof. Ernesto Di Maio U. Naples Federico II

Fit Parameters of PC-SAFT Model to Solubility Measurements

Use linear regression on PC-SAFT parameters N, σ, ϵ, k to fit solubility measurements for each polyol for different p, T

CO_2 Solubility in PPG, 1000 g/mol

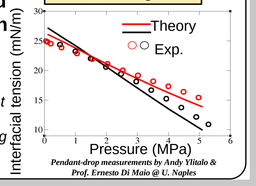


Measurements by Dr. Jacob Crodtwaite @ Dow, Midland and Andy Ylitalo & Prof. Ernesto Di Maio @ U. Naples

Validate DFT Model Against Measured Interfacial Tension

Predictions of interfacial tension by DFT model using PC-SAFT parameters are consistent with experimental measurements, supporting the validity of this model

Interfacial Tension PPG, 1000 g/mol



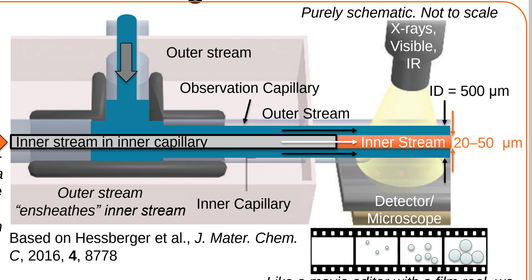
Pendant-drop measurements by Andy Ylitalo & Prof. Ernesto Di Maio @ U. Naples

Instrument Development for "Seeing" Bubble Nucleation

Microfluidic Hydrodynamic-focusing: *A "Film Reel" of Bubble Nucleation*

Initially developed to watch protein folding with x-rays, hydrodynamic-focusing effectively creates a "film reel" of fast (~millisecond) kinetics along the physical length of a microfluidic channel. Here, the inner stream of interest passes through a tee junction from within a small capillary. The outer stream ensheathes this capillary and, later, the inner stream, protecting it from the effects of the walls of the channel, essential for preventing premature bubble nucleation.

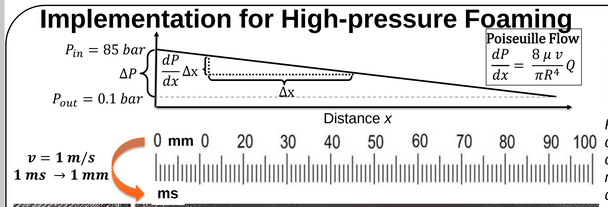
Purely schematic. Not to scale



Based on Hessberger et al., *J. Mater. Chem. C*, 2016, **4**, 8778

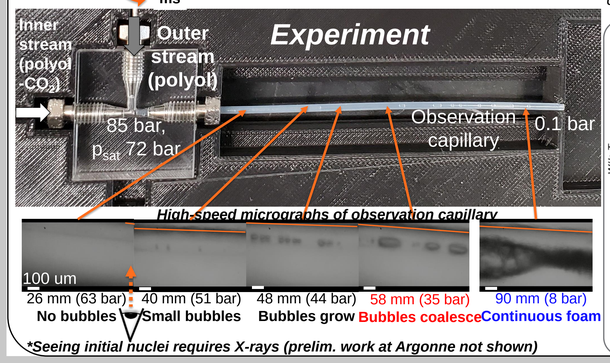
Like a movie editor with a film reel, we can scrutinize each moment of bubble nucleation as long as desired

Implementation for High-pressure Foaming



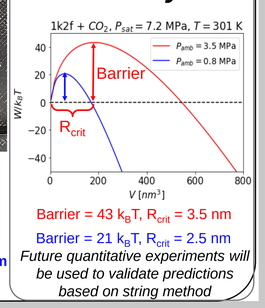
Linear pressure drop is predictably governed by Poiseuille flow since flow behavior is dominated by an incompressible outer stream

Re << 1 due to microfluidic dimensions ensures laminar flow at constant velocity, ensuring the nucleation time is proportional to distance along the channel



**Seeing initial nuclei requires X-rays (prelim. work at Argonne not shown)*

Theory



Barrier = 43 k_BT, R_{crit} = 3.5 nm

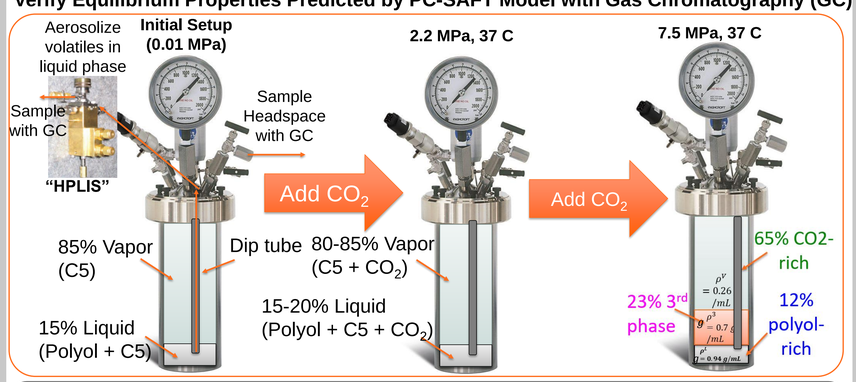
Barrier = 21 k_BT, R_{crit} = 2.5 nm

Future quantitative experiments will be used to validate predictions based on string method

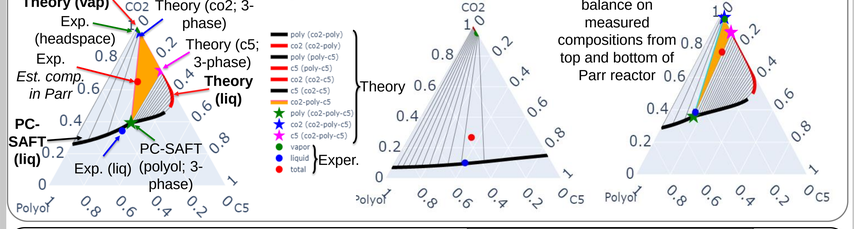
Predicting Effect of "C5" on Bubble Nucleation

**Internship at Dow, Lake Jackson, TX 9/19-10/19*

Verify Equilibrium Properties Predicted by PC-SAFT Model with Gas Chromatography (GC)

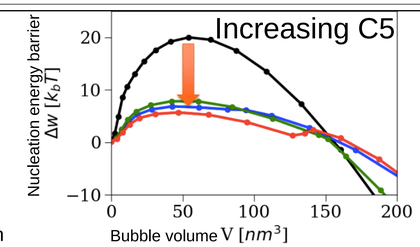


Ternary Phase Diagrams with Measured and Predicted Compositions



Predicted Nucleation Barrier by String Method Model Based on PC-SAFT Parameters Validated by GC Measurements Above

1) Increasing C5 reduces nucleation barrier dramatically (4x)
2) Above threshold C5, nucleation occurs in two steps: liquid-liquid separation followed by vaporization



Conclusions: *Technical*

- Models based on PC-SAFT and DFT predict interfacial properties essential for bubble nucleation models in agreement with measurements
- Preliminary results from microfluidic hydrodynamic-focusing suggest novel method for measuring bubble nucleation to validate string method predictions
- Experiments support accuracy of extension of model to ternary system; model predicts substantial reduction in bubble nucleation with addition of C5

Conclusions: *Personal*

- The Kornfield group has supported my collaboration with leading scientists within Caltech and around the world (U. Naples, Dow, and Argonne)
- Collaboration with industry (Dow) connected me with over a dozen industrial experts to design unique instrumentation for fundamental scientific study
- Theory and experiment beautifully support each other when done in parallel

References

1. Pastore Carbone, Di Maio, Iannace, and Mensitieri, *Simultaneous experimental evaluation of solubility, diffusivity, interfacial tension and specific volume of polymer/gas solutions*, 2011, *Polymer Testing*, **30**, 303-309
2. Xu, Cristancho, Costeux, and Wang, *Bubble nucleation in polymer-CO2 mixtures,* 2013, *Soft Matter*, **9**, 9675-9683
3. Pollack, Tate, Darnton, Knight, Gruner, Eaton, and Austin, *Compactness of the denatured state of a fast-folding protein measured by submillisecond small-angle x-ray scattering,* 1999, *Biophysics*, **96**, 10115-10117