

## Table of Contents

|  |       |
|--|-------|
| Acknowledgments . . . . .  | iii   |
| Abstract . . . . .   | xi    |
| Table of Contents . . . . .  | xi    |
| List of Illustrations . . . . .  | xvi   |
| List of Tables . . . . .   | xxiii |
| Nomenclature . . . . .   | xxiv  |
| Chapter I: Introduction . . . . .  | 1     |
| I.1    The Birth of a Bubble . . . . .   | 1     |
| I.2    The Many Causes of Bubble Nucleation . . . . .  | 2     |
| I.3    Foams: When Many Bubbles Collide . . . . .  | 5     |
| I.4    Bubble Nucleation: Many Models, Few Measurements . . . . .  | 24    |
| I.5    Summary of Contents . . . . .   | 32    |
| Chapter II: Know Mother Best: Measurement and Modeling of the Properties<br>of the Mother Phase Relevant to Bubble Nucleation . . . . .                                | 42    |
| II.1    Gravimetry–Axisymmetric Drop Shape Analysis (G-ADSA) Mea-<br>sures Physical Properties of Polyol–CO <sub>2</sub> Mixtures . . . . .                            | 44    |
| II.2    G-ADSA Measurements: Effects of Pressure and Temperature . . . . .   | 48    |
| II.3    Discussion: Competition Between CO <sub>2</sub> -philicity and Mixing En-<br>tropy Underlies CO <sub>2</sub> Solubility Maximum in Polyether Polyols . . . . . | 53    |
| II.4    Thermophysical Measurements Provide the Basis for Fitting Em-<br>pirical Parameters of Thermodynamic Models . . . . .  | 59    |
| II.5    Recommendation for Future Work . . . . .   | 65    |
| II.S1   Gravimetry–Axisymmetric Drop Shape Analysis (G-ADSA) . . . . .   | 70    |

|   |   |     |
|---|---|-----|
| II.S2   | Estimate Effects of Temperature and Molecular Weight on CO <sub>2</sub> Solubility in 4.7-functional Polyol . . . . . | 79  |
| II.S3   | Comparison of G-ADSA Measurements to Literature . . . . .   | 83  |
| II.S4   | Sensitivity of PC-SAFT and DFT Models to Variations in Parameters . . . . .   | 87  |
| II.S5   | DFT Predicts Non-monotonic CO <sub>2</sub> Concentration Profile . . . . .  | 89  |
| Chapter III: A Bubble Is Born (Nucleated): Microfluidic Flow Focusing Reveals Early Stages of Bubble Growth . . . . . |   |     |
| III.1   | Studying Homogeneous Bubble Nucleation: Challenges and Solutions . . . . .  | 94  |
| III.2   | High-pressure Microfluidic Hydrodynamic Focusing Localizes Supersaturation in Space and Time . . . . .                | 99  |
| III.3   | High-speed Optical Microscopy Captures Early Bubble Growth . . . . .  | 109 |
| III.4   | Recommendations for Future Work . . . . .   | 113 |
| III.S1  | Flow in Microfluidic Sheath Flow . . . . .  | 125 |
| III.S2  | Parameter Selection . . . . .   | 131 |
| III.S3  | Materials for Fabrication of Flow-focusing Apparatus . . . . .  | 134 |
| III.S4  | High-pressure Microfluidic Flow-focusing: Device Fabrication . . . . .  | 134 |
| III.S5  | Other Device Designs . . . . .  | 137 |
| III.S6  | Other Methods Considered for Observing Early Bubble Growth . . . . .  | 138 |
| Chapter IV: Baby Videos: High-speed Optical Microscopy Observes Early Growth of Bubbles . . . . .                     |   |     |
| IV.1  | Image Processing Detects, Tracks, and Measures Bubbles . . . . .  | 148 |
| IV.2  | Recommendations for Further Improvements . . . . .  | 156 |
| Chapter V: Extrapolating Beyond the Limits of Optical Microscopy: Transport Model of Bubble Growth . . . . .          |   |     |
| V.1   | Models of Bubble Growth in Supersaturated Liquids . . . . .   | 160 |

|   |  |     |
|---|--|-----|
| V.2   | Modified Epstein–Plesset Model Fits Measured Bubble Growth   | 165 |
| V.3   | Fitting Model to Data to Extrapolate Bubble Growth Back to Its Birth                                   | 173 |
| V.4   | Bubble Nucleation Can Be Estimated Accurately with $R \propto (t - t_{nuc})^{1/2}$                     | 177 |
| V.5   | Recommended Future Work  | 180 |
| Chapter VI: The Nucleation Nursery  |  | 184 |
| VI.1  | Time between Nucleation Events Described by Poisson Statistics   | 186 |
| VI.2  | Estimation of Nucleation Rate vs. Pressure Indicates Rapid Onset of Bubble Nucleation                  | 190 |
| VI.3  | Model of Bubble Nucleation Energy Barrier by Applying the String Method to a Density Functional Theory | 195 |
| VI.4  | String Method Model Can Be Fit to Measured Nucleation Rate While Classical Nucleation Theory Cannot Be | 199 |
| VI.5  | Recommendations for Future Work  | 202 |
| Chapter VII: Other Mothers: Effects of Additives to the Mother Phase on Bubble Nucleation |  | 206 |
| VII.1   | Adding Cyclopentane Dramatically Increases Bubble Nucleation in Polyol–CO <sub>2</sub> Foam            | 208 |
| VII.2   | String Method Based on DFT Predicts Two-stage Bubble Nucleation with Cyclopentane                      | 212 |
| VII.3   | Adding Cyclopentane Opens Up Three-phase Region  | 218 |
| VII.4   | Future Work  | 230 |
| VII.S1  | Further Discussion of Experimental Apparatus   | 238 |
| VII.S2  | Validation of Sampling Method  | 238 |
| VII.S3  | Analysis for Estimating Composition of Each Phase from Sampling Measurements                           | 242 |

|               |  |     |
|---------------|--|-----|
| VII.S4        | PC-SAFT Model Details . . . . .  | 247 |
| Chapter VIII: | All Grown Up: Leaving the Nest . . . . .                                       | 248 |
| VIII.1        | Bubbles Elongate Upon Facing Viscous Resistance from Outer<br>Stream . . . . . | 249 |
| VIII.2        | Formation of the Wake . . . . .  | 256 |
| VIII.3        | Ripening and Coalescence . . . . .   | 262 |
| VIII.4        | Stream Instabilities . . . . .   | 264 |
| VIII.S1       | Stagnation of Bubbles . . . . .  | 269 |
| VIII.S2       | Nucleation of Bubbles in the Wake of an Elongated Bubble . . .                 | 270 |

## List of Illustrations

| <i>Number</i>   | <i>Page</i> |
|---|-------------|
| I.1 Schematic of three stages of bubble nucleation: supersaturation of mother phase, nucleation, and growth . . . . .   | 2           |
| I.2 Comparison of measurement of nucleation from pockets of trapped gas and homogeneous bubble nucleation . . . . .   | 4           |
| I.3 Comparison of thermal conductivity of different thermally insulating foams as well as polyurethane foams blown with different blowing agents broken down by mode of heat transfer . . . . . | 8           |
| I.4 Depiction of absorption of infrared radiation by “struts” in polyurethane foam matrix . . . . .   | 9           |
| I.5 Radiative thermal conductivity of foam as a function of cell size . . .   | 10          |
| I.6 Schematic of reduction in cell size needed to reduce thermal conductivity of polyurethane foams . . . . .   | 11          |
| I.7 Temperature and height of rigid polyurethane foam over time during production . . . . .   | 13          |
| I.8 Difference in nucleation of bubbles in contact with surface and in bulk of polystyrene foam blown with blend of CO <sub>2</sub> and N <sub>2</sub> . . . . .                                | 17          |
| I.9 Schematic of polyurethane foaming reaction . . . . .  | 19          |
| I.10 Schematic of polyurethane foaming reaction . . . . .   | 20          |
| I.11 Thermal conductivity of gases decreases with molecular weight . . .  | 21          |
| I.12 Model of reversible work to form bubble embryo based on classical nucleation theory . . . . .  | 27          |
| I.13 Roadmap of the cooperation between experiments and theory to understand bubble nucleation . . . . .  | 33          |

|       |   |    |
|-------|---|----|
| II.1  | Carbon dioxide solubility vs. pressure and temperature . . . . .  | 49 |
| II.2  | Non-monotonic specific volume of polyol–CO <sub>2</sub> mixture vs. pressure .  | 50 |
| II.3  | Interfacial tension of polyol–CO <sub>2</sub> mixture vs. pressure, solubility . .  | 51 |
| II.4  | Diffusivity of CO <sub>2</sub> in polyol vs. pressure . . . . .   | 52 |
| II.5  | CO <sub>2</sub> solubility in polyol–CO <sub>2</sub> mixture decreases with number of<br>hydroxyl groups on polyol . . . . .            | 56 |
| II.6  | CO <sub>2</sub> solubility in polyol–CO <sub>2</sub> mixture for two difunctional polyols<br>with different molecular weights . . . . . | 57 |
| II.7  | Non-monotonic Henry’s constant for CO <sub>2</sub> solubility in polyol with<br>molecular weight . . . . .                              | 58 |
| II.8  | Schematic of PC-SAFT model for polyol and CO <sub>2</sub> . . . . .   | 59 |
| II.9  | PC-SAFT model fits measured CO <sub>2</sub> solubility . . . . .  | 61 |
| II.10 | Schematic of DFT model . . . . .  | 62 |
| II.11 | DFT predictions of interfacial tension in polyol–CO <sub>2</sub> mixtures vali-<br>dated against G-ADSA measurements . . . . .          | 63 |
| II.12 | PC-SAFT predictions of specific volume of polyol–CO <sub>2</sub> mixture vs.<br>pressure . . . . .                                      | 64 |
| II.S1 | Swelling of Teflon rod from CO <sub>2</sub> absorption . . . . .  | 70 |
| II.S2 | Schematic of diffusion into a slab . . . . .  | 73 |
| II.S3 | Transient sample mass in G-ADSA with example square-root and<br>exponential fits for estimating CO <sub>2</sub> diffusivity . . . . .   | 77 |
| II.S4 | Plots showing the reproducibility of G-ADSA measurements . . . . .  | 80 |
| II.S5 | Model effects of temperature and molecular weight on CO <sub>2</sub> solubility<br>in 4.7-functional polyol . . . . .                   | 81 |
| II.S6 | Method of estimating effect of molecular weight on CO <sub>2</sub> solubility<br>in 4.7-functional polyol . . . . .                     | 82 |

|        |   |     |
|--------|---|-----|
| II.S7  | Comparison of measurements of CO <sub>2</sub> solubility in PPG by G-ADSA and by FTIR reported in the literature . . . . .                            | 84  |
| II.S8  | Comparison of measurements of CO <sub>2</sub> solubility in polyol by G-ADSA and by similar method reported in the literature . . . . .               | 85  |
| II.S9  | Comparison of measurements of specific volume of polyol–CO <sub>2</sub> mixtures by G-ADSA and by similar method reported in the literature . . . . . | 85  |
| II.S10 | Comparison of measurements of diffusivity of CO <sub>2</sub> in polyol by G-ADSA and by similar method reported in the literature . . . . .           | 86  |
| II.S11 | Henry’s constant for polyol–CO <sub>2</sub> mixtures from G-ADSA and literature   | 87  |
| II.S12 | Sensitivity of PC-SAFT model predictions to variations in its parameters  | 88  |
| II.S13 | Plots comparing PC-SAFT model predictions of measured thermo-physical parameters with two sets of parameters . . . . .                                | 90  |
| II.S14 | Density profile of polyol and CO <sub>2</sub> at interface between liquid and vapor phases predicted by DFT . . . . .                                 | 91  |
| III.1  | Schematic of microfluidic channel showing flow profile . . . . .  | 100 |
| III.2  | Schematic of microfluidic channel showing pressure profile . . . . .  | 103 |
| III.3  | Image of microfluidic channel with example images of bubbles . . . . .  | 105 |
| III.S1 | Shear rheometry of polyols . . . . .  | 125 |
| III.S2 | Width of inner stream vs. flow rate in flow-focusing channel . . . . .  | 130 |
| III.S3 | Comparing observation capillary with and without lensing effects . . . . .  | 131 |
| III.S4 | Dimensional sketch of acrylic block for microfluidic flow-focusing instrument . . . . .   | 136 |
| III.S5 | SAXS of SiO <sub>2</sub> nanoparticles in water . . . . .   | 140 |
| III.S6 | Comparison of drift in SAXS signal to noise in background of pure water . . . . .   | 141 |
| III.S7 | Comparison of SAXS signal, background and noise of SiO <sub>2</sub> nanoparticles in water . . . . .  | 142 |

|        |   |     |
|--------|---|-----|
| III.S8 | Schematic of proposed laser scattering setup . . . . .  | 144 |
| IV.1   | Comparison of background-subtraction methods . . . . .  | 149 |
| IV.2   | Schematic of hysteresis thresholding . . . . .  | 151 |
| IV.3   | Demonstration of image segmentation and measurement of bubble size  | 152 |
| IV.4   | Schematic depicting object tracking algorithm . . . . .   | 153 |
| IV.5   | Demonstration of image segmentation and measurement of bubble size  | 154 |
| V.1    | Schematic showing how the spatial resolution of microscopy prevents<br>the direct observation of bubble nucleation with the present technique                                       | 159 |
| V.2    | Model of bubble growth excluding convection significantly underes-<br>timates measured bubble growth . . . . .  | 164 |
| V.3    | Schematic of Epstein–Plesset model of bubble growth based on Fick’s<br>Laws . . . . .   | 166 |
| V.4    | Schematic of flow-focusing channel used for solving flow . . . . .  | 167 |
| V.5    | Example calculation showing how to estimate the inner stream viscosity  | 169 |
| V.6    | Schematic of numerical algorithm for computing bubble growth with<br>modified Epstein–Plesset model . . . . .   | 171 |
| V.7    | Model of bubble growth based on Epstein–Plesset model multiplied<br>by an empirical factor accounting for convection and depletion effects<br>fits measured bubble growth . . . . . | 176 |
| V.8    | Comparison of bubble growth and nucleation time predicted by fitting<br>asymptotic square-root model vs. modified Epstein–Plesset model . .   | 179 |
| VI.1   | Distribution of times between nucleation events follows exponential<br>decay expected for a Poisson process . . . . .   | 188 |
| VI.2   | Binned counts of bubble nucleation along the observation capillary<br>converted to nucleation rates . . . . .   | 191 |



|       |  |     |
|-------|--|-----|
| VI.3  | Comparison of nucleation rates estimated using the square-root and modified Epstein–Plesset models of bubble growth shows little discrepancy . . . . .   | 194 |
| VI.4  | Schematic of string method applied to DFT and example predictions of nucleation energy barrier and density profiles along the nucleation pathway . . . . .   | 196 |
| VI.5  | Two sets of PC-SAFT parameters that lead to accurate models of CO <sub>2</sub> solubility and interfacial tension result in drastically different predictions of the nucleation barrier . . . . .      | 198 |
| VI.6  | Comparison of estimated nucleation rate from experiments to fitted string method model shows agreement . . . . .   | 200 |
| VII.1 | Comparison of bubble nucleation rate vs. supersaturation between a PPG–CO <sub>2</sub> mixture and a PPG–cyclopentane–CO <sub>2</sub> mixture prepared and flowed under identical conditions . . . . . | 209 |
| VII.2 | Example of exponential decay of incubation time of bubbles in a PPG–cyclopentane–CO <sub>2</sub> mixture and comparison of estimated nucleation rate with that obtained by counting bubbles . . . . .  | 211 |
| VII.3 | Nucleation energy barrier significantly reduced when addition of cyclopentane opens up two-stage nucleation pathway . . . . .  | 214 |
| VII.4 | First stage of two-stage nucleation upon addition of cyclopentane is liquid–liquid phase separation . . . . .  | 215 |
| VII.5 | Density profiles of nucleating bubble with cyclopentane show transition from liquid-like to vapor-like density . . . . .   | 217 |
| VII.6 | Example of how to read a Gibbs triangle . . . . .  | 220 |
| VII.7 | Prediction by PC-SAFT model of phase behavior of ternary mixture of polyol, CO <sub>2</sub> , and cyclopentane shows three-phase coexistence . . .   | 221 |

|        |   |     |
|--------|---|-----|
| VII.8  | Method for demonstrating three-phase coexistence by pressurizing ternary mixture with CO <sub>2</sub> . . . . .   | 222 |
| VII.9  | Schematic of apparatus for sampling light and dense phases in high-pressure chamber . . . . .   | 223 |
| VII.10 | Photograph of high-pressure sampling apparatus . . . . .  | 225 |
| VII.11 | Schematic showing difficulty of sampling a third phase of intermediate density in high-pressure vessel . . . . .  | 226 |
| VII.12 | Missing mass in composition measurements provides indirect evidence of formation of third phase . . . . .   | 227 |
| VII.13 | Comparison of measured and predicted compositions at three-phase coexistence and estimated volume of each phase . . . . .                                     | 228 |
| VII.14 | Depiction of method of two-stage foaming to enhance bubble nucleation   | 231 |
| VII.15 | Proposed experiments with isocyanate . . . . .  | 232 |
| VII.S1 | Photograph showing alternative view of high-pressure sampling apparatus . . . . .   | 239 |
| VII.S2 | Calibration curves of gas chromatograph (GC) . . . . .  | 240 |
| VII.S3 | Measurements of CO <sub>2</sub> solubility in polyol with high-pressure GC sampling to validate against G-ADSA . . . . .                                      | 241 |
| VII.S4 | Estimation of saturation time of gas in polyol in Parr reactor . . . . .  | 241 |
| VIII.1 | Superimposed snapshots showing a bubble grow spherically, elongate along the flow axis, and leave a wake upon reaching the size of the inner stream . . . . . | 250 |
| VIII.2 | Bubble growth rate transitions from square-root to exponential dependence on time upon reaching size of inner stream . . . . .                                | 251 |
| VIII.3 | Still frames show small bubbles stagnate in the thin film between an elongated bubble and the outer stream as the elongated bubble passes by them . . . . .   | 253 |

|         |   |     |
|---------|---|-----|
| VIII.4  | Schematic showing that the displacement of fluid by an elongating bubble under confinement causes the bubble to accelerate faster than the surrounding medium . . . . . | 254 |
| VIII.5  | Speed of bubbles increases with length and rate of growth . . . . .   | 255 |
| VIII.6  | Example of bubbles nucleating along the “trail” at the center of the wake left behind by an elongated bubble . . . . .  | 258 |
| VIII.7  | Schematic of the depletion layer along the head of an elongated bubble  | 259 |
| VIII.8  | Schematic of the depletion layer past the tail of an elongated bubble and its role in the wake . . . . .  | 260 |
| VIII.9  | Proposed relative concentrations of CO <sub>2</sub> in different regions of the wake left behind by an elongated bubble . . . . .                                       | 261 |
| VIII.10 | Sequence of images shows two bubbles in contact merge through ripening . . . . .  | 263 |
| VIII.11 | Comparison of instability driven by viscosity difference with literature  | 265 |
| VIII.12 | Pearls-on-a-string fluid instability . . . . .  | 267 |
| VIII.S1 | Still frames show how small bubbles in the outer stream slow down almost to stagnation when an elongated bubble passes by them . . . .                                  | 269 |
| VIII.S2 | Depiction of bubble nucleation in the wake of an elongated bubble followed by merging and more nucleation in the wake . . . . .   | 270 |

## List of Tables

| <i>Number</i>   | <i>Page</i> |
|---|-------------|
| I.1 Comparison of features of studies of polyurethane foaming . . . . .                                       | 18          |
| II.1 Polyol properties . . . . .  | 44          |
| II.2 PC-SAFT parameters fitted to solubility measurements . . . . .   | 60          |
| III.1 Objective lens properties . . . . .   | 110         |
| III.S1 Materials to fabricate flow-focusing channel . . . . .   | 135         |
| III.S2 Materials to encase observation capillary in optical adhesive . . . . .                                | 138         |
| VII.S1 Comparison of CO <sub>2</sub> solubility measured with high-pressure GC apparatus and G-ADSA . . . . . | 240         |
| VII.S2 PC-SAFT parameters for cyclopentane . . . . .  | 247         |

## Nomenclature

- DFT.** Classical Density Functional Theory. A framework based on electronic DFT for modeling the spatial variation in the number density of classical particles by minimizing the free energy density functional of the density profile of these particles.
- Difunctional.** Describes a polyol that has two hydroxyl groups (OH) per polymer chain.
- Foam.** A gas dispersed in a liquid or solid matrix.
- Functionality.** Average number of hydroxyl functional groups per polymer chain..
- Gravimetry–Axisymmetric Drop Shape Analysis (G-ADSA).** A technique that combines precise measurement of the weight of a liquid–gas mixture using a sensitive balance (gravimetry) and image analysis of a pendant drop of the same mixture (axisymmetric drop shape analysis) to measure gas solubility, specific volume, gas diffusivity, and interfacial tension simultaneously.
- Harvey Nucleus.** A pocket of vapor trapped in the crevice of a solid surface that produces bubbles without nucleation as the pocket of vapor grows large enough for a bubble to detach.
- Heterogeneous Nucleation.** Nucleation that occurs with the aid of a surface, often in a niche or crack within it. The aid of the surface reduces the supersaturation required for nucleation.
- Homogeneous Nucleation.** Nucleation that occurs in the bulk phase. Without the aid of a surface, the supersaturation required for nucleation is much greater than for heterogeneous nucleation.
- ISCO Pump.** A brand of high-pressure syringe pump providing high-precision, pulseless flow. Commonly used in high-pressure microfluidics and supercritical CO<sub>2</sub> applications.
- Knudsen Effect.** Reduction in the thermal conductivity of a gas as a result of confinement below its mean free path, which effectively shortens the mean free path.
- Mother Phase.** The medium from which a new phase can nucleate upon supersaturation.
- Nucleation.** The local formation of a new phase through a first-order phase transition, which requires the system to overcome a free energy barrier.

**PC-SAFT.** Perturbed Chain–Statistical Associating Fluid Theory, an equation of state published by Gross and Sadowski in *Industrial and Engineering Chemistry Research* (2001).

**Physical Blowing Agent (PBA).** A volatile, non-reactive compound that vaporizes upon modest heating to generate a foam.

**PPG.** Polypropylene glycol.

**RMSSFE.** Root mean signed squared fractional error, the mean of each squared error multiplied by the sign of the error.

**RPUF.** Rigid Polyurethane Foam, a foam commonly used for thermal insulation in refrigeration units, coolers, and buildings.

**Small-Angle X-ray Scattering (SAXS).** X-ray scattering technique that detects only X-rays scattered at angles between  $0.1^\circ$ – $10^\circ$  from the incident beam axis. These angles correspond to features on the length scale of 1–100 nm.

**String Method.** A method for identifying the most probable path between two states in a free energy landscape by minimizing the free energy barrier along that path. Often described as the result of pulling a string taut between the two states.